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EFFECT OF SELECTED GEOLOGY-SOIL COMPLEXES ON WATER QUALITY OF THE LITTLE BLACK FORK CREEK

Completion Report

by

Stanley L. Ponce, Kerry D. Sundeen and W. David Striffler
Department of Earth Resources
Colorado State University
Fort Collins, Colorado 80522

submitted to

U.S. Forest Service
USDA
Northeastern Forest Experiment Station

The work upon which this report is based was supported with funds provided by the U. S. Forest Service, USDA, Northeastern Forest Experiment Station, Research Work Unit FS-NE-1602.

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ABSTRACT

The purpose of this study was to interpret the chemical water quality of an undisturbed Appalachian watershed in relation to the soil and geologic complexes exposed and to develop a method for the prediction of baseline stream chemistry as a function of soil and geologic complexes. Water quality data were collected and analyzed by the U. S. Forest Service over a two and one-half year period for almost 50 sites within a 1230 ha undisturbed basin in northeastern West Virginia. Six separate soil and geologic complexes were exposed on the watershed.

Cluster analysis was applied to the data set to group sites with similar water quality. The stream chemistry of each group of similar sites was then related to the soil and rock complexes exposed. Waters associated with the sandstone Pottsville and Pocono complexes were determined to be strongly acid with relatively low specific conductance. Waters draining the carbonate Greenbriar complex were typified by a basic pH and relatively higher alkalinity, calcium and magnesium concentrations. Stream chemistry of sites draining the Mauch Chunk complex also exhibited carbonate characteristics while waters from the Hampshire complex were low in specific conductance with slightly increased potassium concentrations.

Specific conductance and pH were selected as the most important parameters to simulate. Prediction techniques were initially based on mass-balance concepts. However, when missing discharge values were synthesized and water quality rating curves developed it was evident that specific conductance and pH were independent of flow. As a result, a simplistic loading function based on an area weighing concept was developed for both specific conductance and pH.

These functions predicted mean conductivity and pH fairly well for the study watershed. When applied to adjacent watersheds, the function results were fairly good for watersheds of similar size or smaller than the Little Black Fork and quite poor for larger watersheds. The functions developed are only first approximations and require further refinement and development.

ACKNOWLEDGEMENTS

The work upon which this report is based was supported with funds provided by the U. S. Forest Service, U.S.D.A. Northeastern Forest Experiment Station, Research Work Unit FS-NE-1602.

The authors would like to express their appreciation to Gerald Aubertin, John Currier and James Patric. Each of these individuals was involved with the design and data collection of the Little Black Fork Study. A special thanks is given to Wayne Patton and L. Eric Siverts of the Watershed Development Group, U. S. Forest Service, and Dale Dunshie of the Monongahela National Forest. The comments and suggestions of each of these individuals were very valuable to us in this study.

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INTRODUCTION

Current water quality legislation, in particular, section 208 of Public Law 92-500, calls for the identification of nonpoint source pollutants by local planning agencies. This legislative directive, coupled with increasing public concern over the quality of our water resources, has put a great demand upon land managers to identify and locate land use activities which degrade water quality by the addition of nonpoint pollutants.

Any land use activity can have a negative impact upon water quality, especially if it results in a disruption of the soil mantle and underlying geologic material. Water moving over or through disturbed land areas often has its chemical properties altered more rapidly and to a greater degree than would occur under natural, undisturbed conditions. An example is the drainage from an open-pit coal mine in the Appalachian region. These mines disturb the soils and rocks present which, in turn, alters the flow and quality of water. Pyritic and other coal-associated materials are often exposed and waters draining these areas may exhibit an extremely acidic condition along with high iron and sulfate concentrations.

Land managers are faced more frequently with the question: "How much of the water quality degradation of a stream is due specifically to management practices applied in the watershed?" This study was initiated by the U. S. Forest Service to address this question. In the Appalachian region severe inorganic water quality degradation may result from management practices. The baseline inorganic water quality is strongly related to the soils and rocks present. It was felt that if an understanding of the effect of the various soils and rock complexes present in the Monongahela National Forest could be defined, methods could be developed to predict baseline water quality for the surface waters in the forest.

A watershed containing the six major surface geologic units and associated soils present in the Monongahela National Forest was located and sampled intensively over a two-year period. The samples were collected, analyzed and compiled by U. S. Forest Service personnel. However, the data were not interpreted, resulting in the initiation of this project.

The specific objective of this study was to analyze the surface water quality data collected by the U. S. Forest Service during the Little Black Fork Study and relate it to the various geologic and soil complexes in the watershed. A secondary objective was to develop a method for the prediction of baseline specific conductance and hydrogen ion activity in stream water.

PAST WORK

Geologic Influence on Water Quality

The weathering of geologic material provides the major supply of ions to natural waters. In general, the chemical and physical characteristics of the rocks control the composition and quantity of dissolved solids in waters draining through them. A detailed discussion of the influence of geology on water quality has been prepared by Hem (1970). This section will simply highlight the general relationships that exist between the major types of rock and the water quality.

Igneous and Metamorphic Rocks

Most water from igneous or metamorphic rocks has good to excellent water quality (Davis and DeWiest, 1966). Rocks of this nature are generally dense, nonwater-bearing structures that are not easily dissolved or weathered, resulting in low dissolved solids concentrations. Water from igneous and metamorphic rocks tends to be of a calcium-magnesium-bicarbonate type, or in the case of acidic volcanic rocks, a sodium-bicarbonate type with relatively large amounts of silica. Poor chemical quality from these rock types occurs near hot springs where water may contain large concentrations of sodium and chloride, or in coastal or desert areas where airborne salts or evaporites are dissolved in surface waters.

Sedimentary Rocks

Contrasts in the chemical quality of water are usually quite marked in the three common groups of sedimentary rocks; shales, carbonates and sandstones (Davis and DeWiest, 1966). Waters from shales commonly contain greater amounts of iron and fluoride, and have a pH typically between 5.5 and 7.0. A lower silica content, a greater amount of calcium and magnesium and pH values above 7.0 are usually associated with carbonates. The water quality of sandstones is somewhat more variable, depending on mineral composition of the rock, adjacent rock types and the depth of the aquifiers.

Prediction of Stream Chemistry from Rock Type

While much work has been done to define qualitative relationships between geology and water quality, few studies have been directed toward the quantification or prediction of stream chemistry as a function of rock type. One such study was made by Miller (1961) for an area of the Sangre de Cristo mountains in New Mexico. The relationship of dissolved solids to drainage area was determined for a sedimentary sandstone, an igneous granite and a metamorphic quartzite enabling the prediction of dissolved solids concentration given the rock type and drainage area (Figure 1). Dissolved solids concentrations were shown to increase from low in small drainage areas to relatively uniform in larger basins. Miller's relationships were developed on watersheds underlain by single rock types and had no applicability to basins of mixed geologic composition.

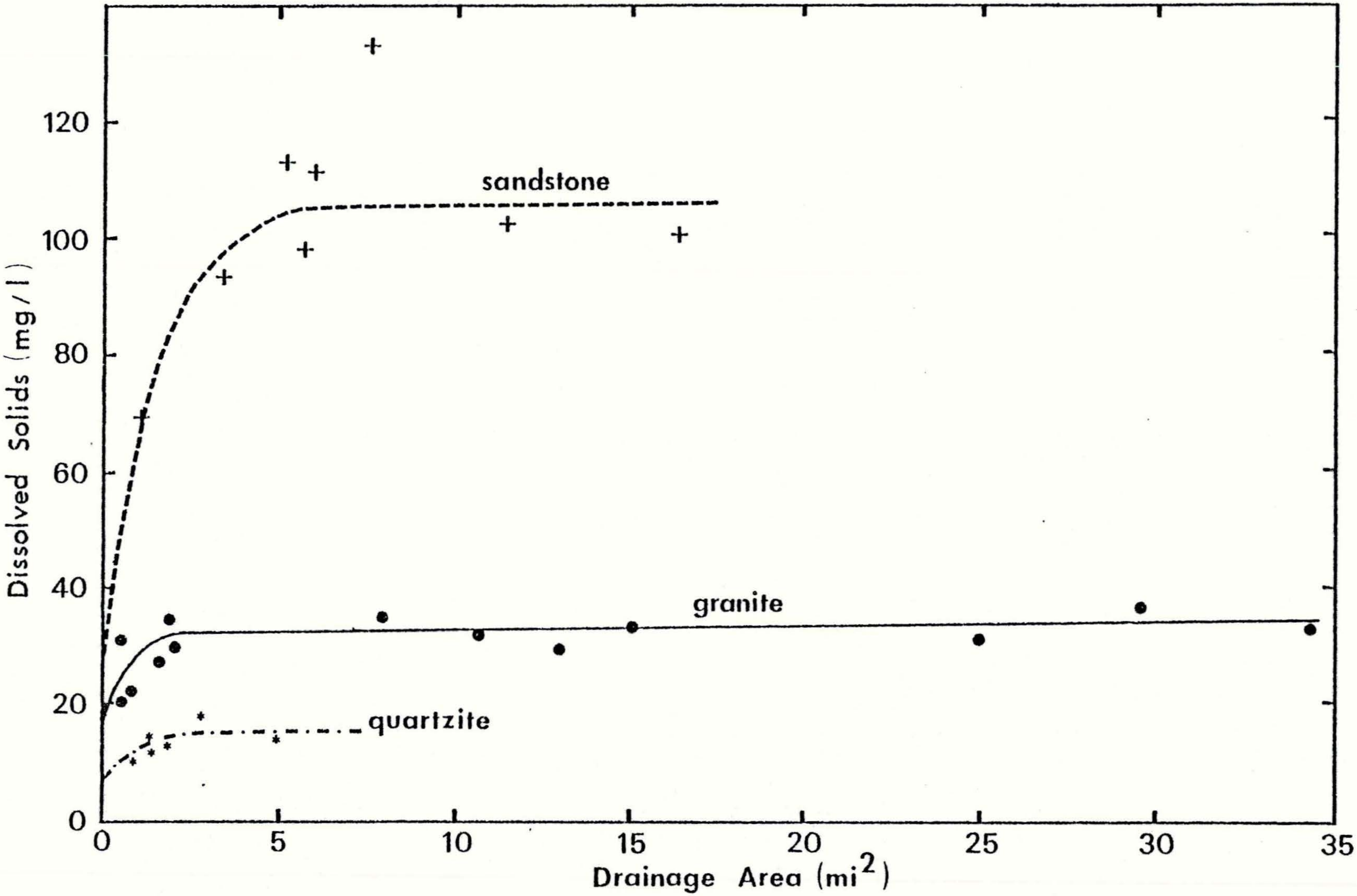

Figure 1. Relationship of dissolved solids to drainage area (after Miller, 1961).

A mass-balanced approach was developed by Ponce and Hawkins (1978) for the estimation of total dissolved solids in the Price River basin of Utah. The model used was

$$TDS_c = K \frac{E_s A}{Q} \qquad [1]$$

where TDS_c is the total dissolved solids concentration corrected for precipitation inputs, A is the area of a geologic type, Q is the volume of overland flow, K is a regression constant and E_s is the dissolved solids supply rate for a specific geologic type. This relation allowed the simulation of a dissolved load for different discharge conditions.

One of the most ambitious attempts to quantify the relationship between geologic type and stream chemistry was made by Haupt and Snyder (1978). A model to simulate specific conductance was developed for 12 watersheds of mixed geologic composition in southwestern Montana. It was assumed that specific conductance represents a composite of ionic contributions from all geologic types present and that the contribution by each geologic formation to the total specific conductance is proportioned to the areal extent of that formation on the watershed. Relationships between specific conductance and discharge were quantified for each watershed in order to simulate specific conductance at a uniform or normalized flow. A discharge of 1.0 CSM, representing base flow, was selected as the normalized discharge. The model

$$SC = \sum_N di_N (g_N) f_N \qquad [2]$$

was used to estimate normalized specific conductance (SC)where di_N is a nondimensional dissolution index for the N^{th} rock type, g_N is the areal proportion of the N^{th} rock type present in the basin and f_N is a function which accounts for variation in the dissolution index. The variation of dissolution indices for the rock types studied is shown in Figure 2. The model simulated normalized specific conductance of the 12 watersheds with good success. It was also applied to fifteen impacted watersheds to estimate which of the basins were yielding dissolved solids in excess of natural rates.

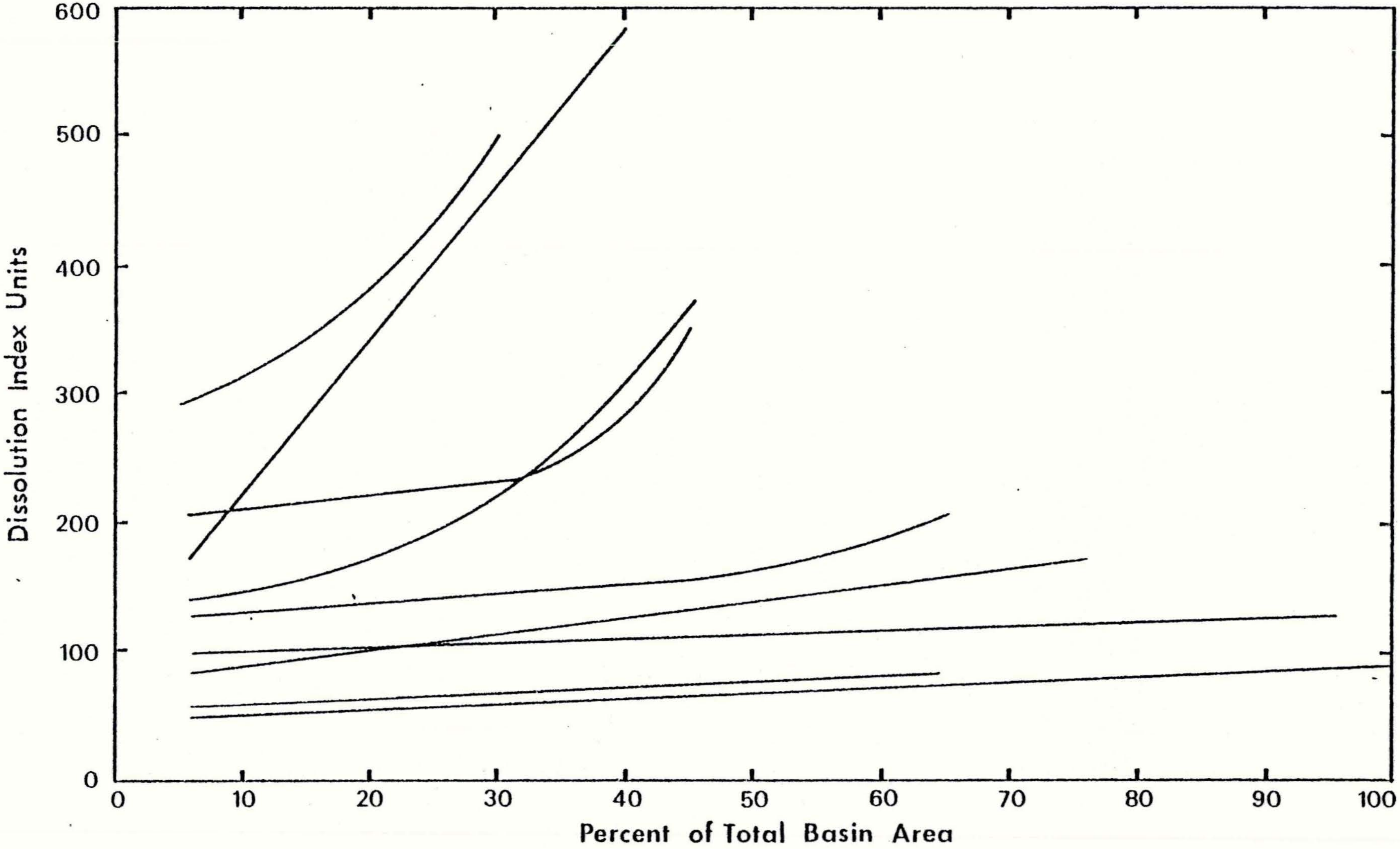

Figure 2. Relation of dissolution indices to percent of total basin area for various geologic types (after Haupt and Snyder, 1978).

STUDY AREA AND DATA BASE

Study Area

General Characteristics

Data for this project were collected by the U. S. Forest Service from the Little Black Fork Watershed, a 1230 ha basin. This watershed was chosen for several reasons. First, all the major surface geologic formations found in the Monongahela National Forest are exposed to some extent on the watershed. Second, it supports a mature hardwood forest typical of the Monongahela National Forest. Third, it has remained virtually undisturbed since the early 1900's with foot trails the only access into it.

The basin is located about 10 km east-northeast of Elkins, West Virginia, (Figure 3) in the Allegheny mountain section of the unglaciated Appalachian Plateau. It is a part of the headwaters of the Monongahela River system and has an elevation range of 595 m at the mouth to 1190 m at the headwaters. The climate of the area is typical of the Allegheny mountain section of Central Appalachia. Average fall and winter precipitation is 22.5 cm and 25.2 cm, respectively (Lee, *et al.*, 1977), and occurs as both rain and snow. In the spring and summer, precipitation generally occurs as rainfall and averages 29.2 cm and 32.7 cm, respectively.

The growing season generally lasts from early May through late October (U. S. Department of Agriculture, 1941). Average seasonal temperatures are: winter, $1^{\circ}C$; spring, $11^{\circ}C$; summer, $22^{\circ}C$; and fall $13^{\circ}C$.

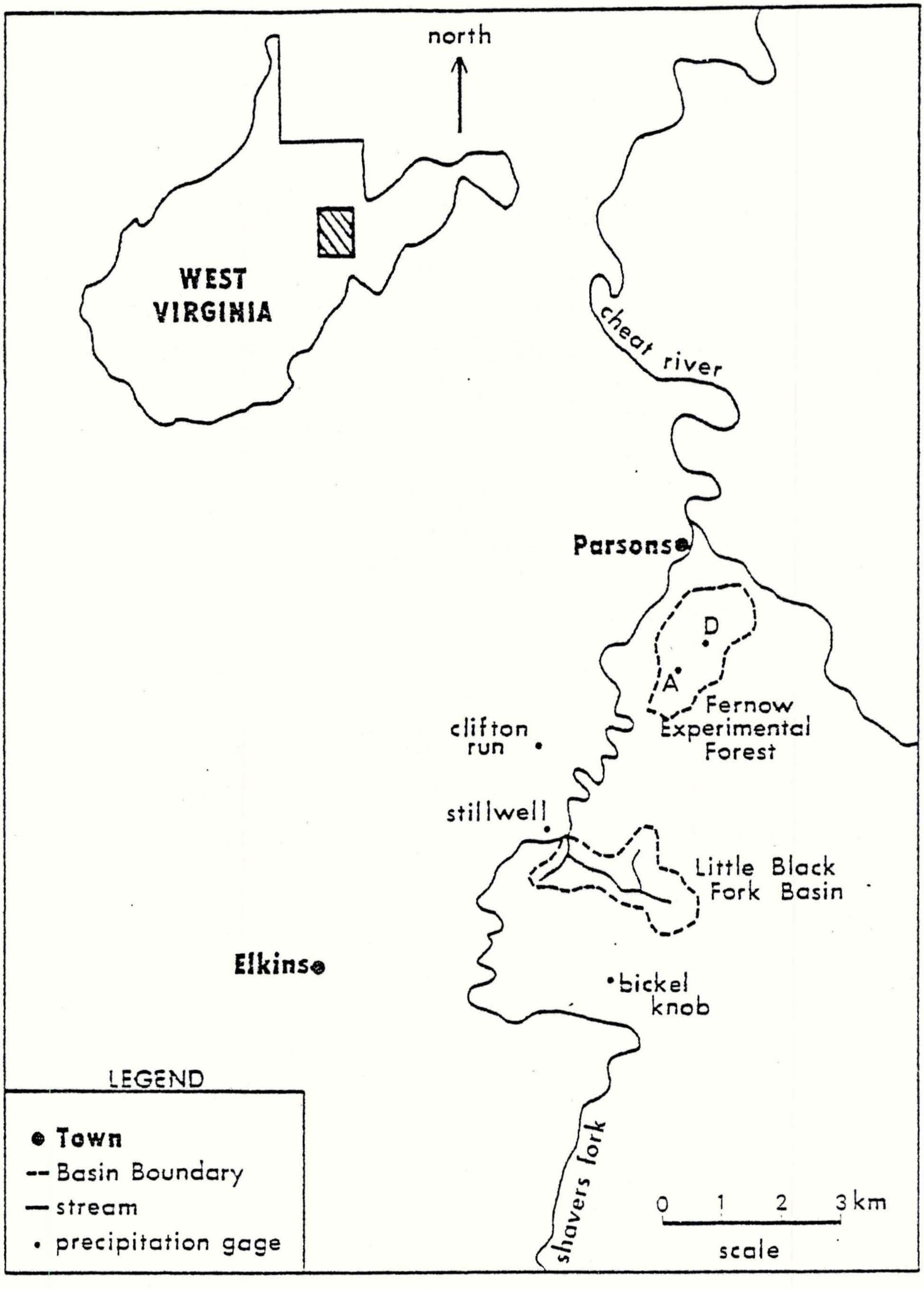
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Figure 3. Location of study area and precipitation gages.

The watershed is covered with a mature stand of Appalachian hardwoods interspersed with conifers. The major tree species present include Maple, Beech, Birch, Black Cherry, Oak, Hickory, Cove Hardwoods and Black and Red Spruce. The watershed experienced a moderate cutting in the early 1900's and has remained virtually undisturbed since.

Streamflow is variable throughout the basin with the main stem of the Little Black Fork being the only perennial stream. Discharge at the mouth of the watershed commonly ranges from 1 to 100 cfs. Streamflow is normally highest in the winter and spring; however, high discharges resulting from storm runoff can occur at any time. Overland flow is minimal, occurring locally on rock outcrops and for short distances on the litter layer. The watershed has a drainage density of 11.2 m/ha and an average mainstream gradient of 16 percent.

Geology

Six major geologic formations are exposed on the watershed. The rock types are sedimentary in origin and were deposited during the Pennsylvanian, Mississippian and Devonian periods (Figure 4). Subsequent uplifting, folding and erosion have molded the formations into the present topography of steep, rugged slopes, narrow valleys and many small, finely dissected watersheds.

Pennsylvanian Period. Only one rock group on the watershed, the Pottsville, was deposited during this period. The Pottsville group is the youngest rock type in the basin, covering nearly 390 ha of the watershed (32 percent of the total area). This rock strata exposed in

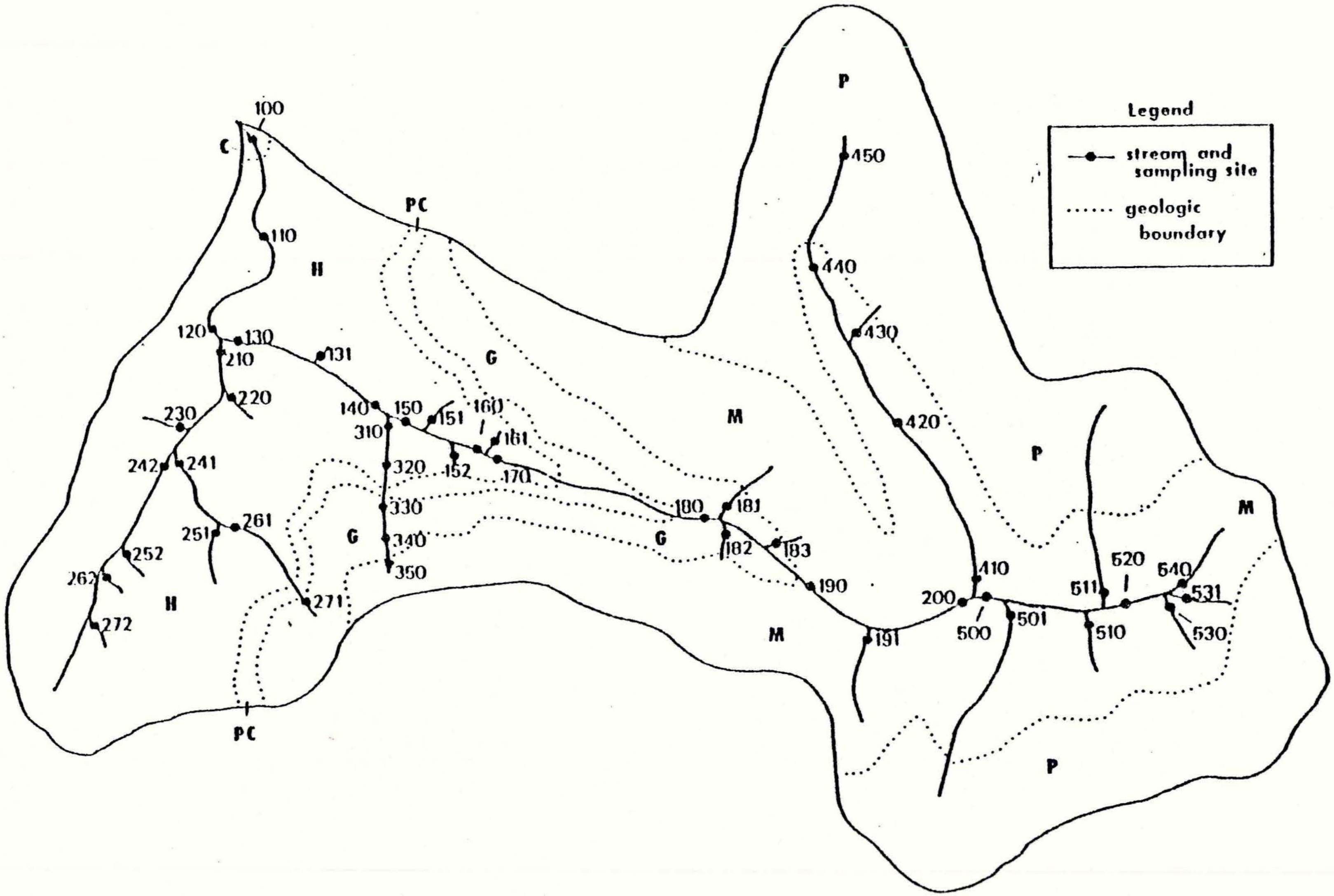
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Figure 4. Sampling sites and exposure of geologic groups: Pottsville (P), Mauch Chunk (M), Greenbriar (G), Pocono (PC), Hampshire (H), and Chemung (C).

the upper portion of the basin, is characterized by a dense sandstone upper layer, overlaying dark or sandy shales with some coals (Reger, Price and Tucker, 1923). In addition to the coal lenses, some pyrite deposits are present. The sandstone members of this rock type are relatively resistant to weathering, which has resulted in a topography of sharp precipices and ledges.

Mississippian Period. Three rock groups on the watershed, the Mauch Chunk, Greenbriar and Pocono, were deposited during the Mississippian Period. The Mauch Chunk group is the youngest member and is exposed on about 400 ha or 33 percent of the total watershed area. It is composed primarily of red shales, with some greenish shales and thin, fine-grained sandstone beds. The ferric iron content of the red shales varies from eight to ten percent. Shales of this group are easily weathered and lead to steep, rounded slopes unlike the ledges associated with the Pottsville group.

Underlying the Mauch Chunk group is the Greenbriar group, having a surface exposure of 100 ha or nine percent of the basin area. This rock type is comprised of several marine limestone beds separated by thin red or gray shale lenses. The limestone strata are generally thin and siliceous near the top of the formation and massive and nearly pure near the base. The Greenbriar group is easily weathered and is characterized by numerous surface depressions and sink holes.

The oldest rock group representing the Mississippian Period is the Pocono. It consists of gray and brown sandstone interspersed with thin shale lenses. Occasional coal deposits are also present. The sandstones of the Pocono group are uneven in texture and support the easily weathered Greenbriar limestone. The Pocono is exposed on about 32 ha or three percent of the watershed surface.

Devonian Period. Below the rocks of the Mississippian Period are those associated with the Devonian Period, the Hampshire and Chemung groups. The Hampshire formation covers 305 ha or 25 percent of the basin area. It is composed of alternating red shale and micaceous sandstone beds. Ferric iron is present in the red shale material. This rock type weathers into concave slopes gentler than those associated with the formations above.

The oldest rock group found on the watershed is the Chemung. It is composed of alternating olive-green shales and fine-grained sandstones. The Chemung is exposed only in a small area (1 ha) at the mouth of the basin.

Soils

The soil series present on the Little Black Fork watershed are the Ernest, Penn, Meckesville, Dekalb and Calvin (Aubertin, 1973). The physical and chemical nature of each series is strongly characteristic of the geologic parent material from which the soil has been derived.

The Ernest series is a deep, moderately well-drained soil which has developed from the New River formation of the Pottsville Group. In general, this series is strongly acidic with moderately low natural fertility. The A horizon is a dark, grayish brown silt loam underlain by a yellow-brownish silty clay loam. Intermittent fragipans are present at a depth of 50 to 75 cm. The Ernest Series is not only found on top of the Pottsville group, but also on Pottsville colluvium overlying the Mauch Chunk group.

The Penn series is derived from shales and siltstones on steep, upland areas underlain by the Mauch Chunk group. In general, it is a well-drained shallow soil, with moderate natural fertility. Textures range from silt loam to silty clay loam.

The Meckesville series is found on the lower, gentler slopes of the Mauch Chunk group. This series is deep and well drained with moderate natural fertility. Textures range from loam to clay-loam. Meckesville soils are typically covered by a thin litter layer and have fragipans at a depth of 65 to 120 cm.

Belmont soils are a well-drained, slightly plastic, calcareous series weathered from the Greenbriar group. Texture ranges from silt-loam to clay-loam. This series has a high natural fertility and is frequently shallow.

The Dekalb series has developed from acidic sandstones in the upland region of the watershed. This series is found immediately above the Pocono group and on ridges and rocky slopes of the Pottsville group. Dekalb soils are well drained, coarse textured and often stony. Fertility is moderately low and depth to bedrock is generally 50 to 100 cm.

The lower portion of the watershed is covered by soils of the Calvin series derived from the Hampshire formation. This series is a deep, loamy-skeletal soil with moderate fertility. Depth to bedrock is 50 to 100 cm.

The soil series on the Little Black Fork Basin occur singlarly or in association with each other (Figure 5).

Data Base

Data collection was initiated on the Little Black Fork Basin in October 1973 through a cooperative effort by the Northeast Forest Experiment Station and the Monongahela National Forest. In order to monitor the water quality of all major waterways and tributaries as well as changes in water quality resulting from passage over and through the various rock types, nearly 50 sampling stations were established on the watershed (Figure 4). The proportion of the drainage area occupied by the various geologic groups and soil associations are given for each sampling station in Table 1.

Grab samples were collected monthly at each sampling station from October 1973 through April 1976, except during times of no streamflow. During some periods of extremely low streamflow, samples were collected by digging a hole in the channel bed and filling a sample bottle with alluvial water (Adams, 1978). Each sample was analyzed for the following chemical and physical parameters on a regular basis: specific conductance, calcium, magnesium, sodium, potassium, iron, nitrate, sulfate, hydrogen ion activity, alkalinity and turbidity. Specific conductance and pH were measured in the field, while all other parameters were analyzed in the laboratory using standard methods (American Public Health Association, 1971).

Discharge was also measured, but not at regular intervals or at all of the sampling stations. Flow measurements were taken at 15 selected

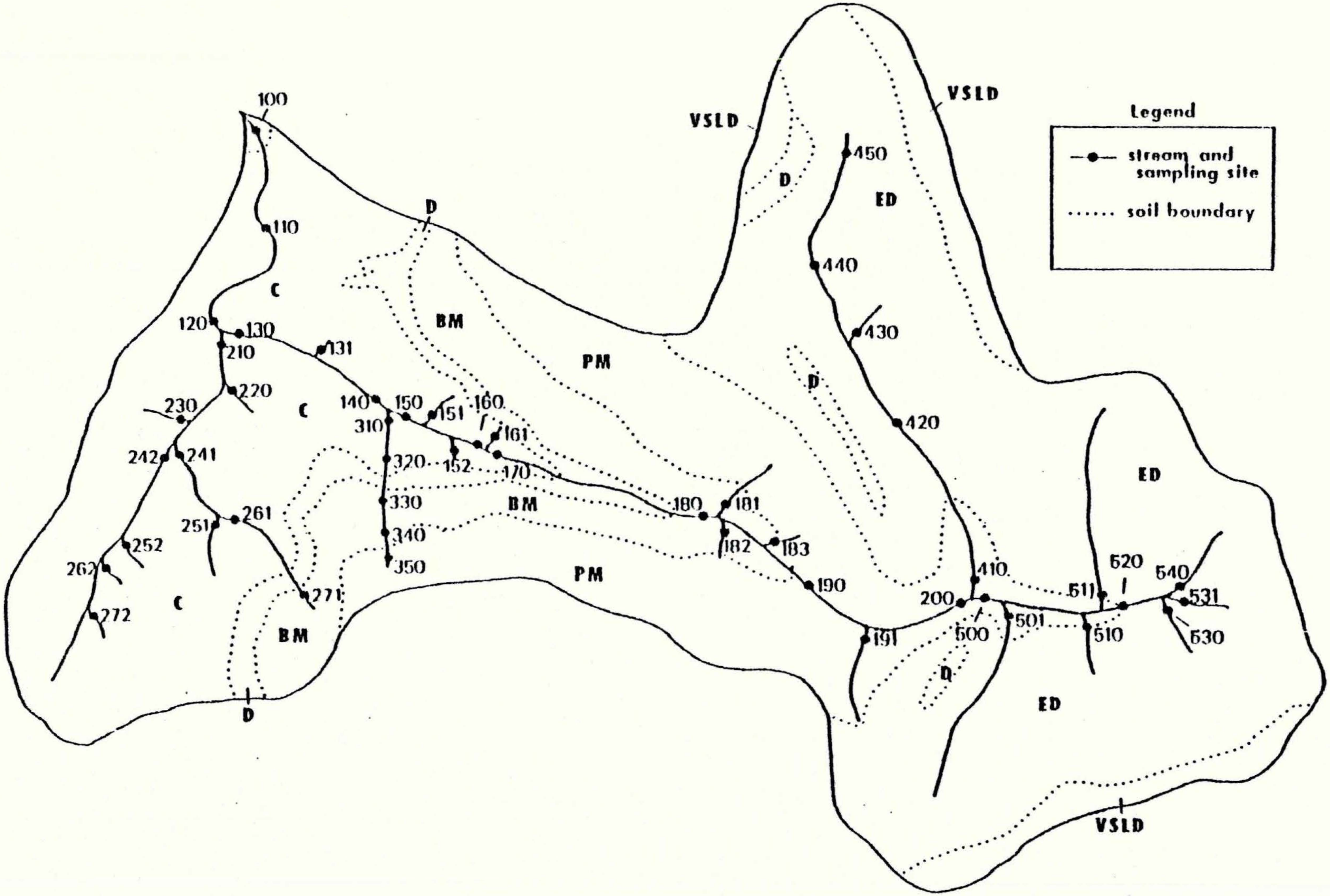
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Figure 5. Sampling sites and exposure of soil associations: Very Stony Land-Dekalb (VSLD), 80% Ernest - 20% Dekalb (ED), 100% Dekalb (D), 50% Penn - 50% Meckesville (PM), 50% Belmont - 50% Meckesville (BM) and 100% Calvin (C).

Table 1. The percent of drainage area occupied by the various geologic types and soil associations for each site.

	GEOLOGY					SOILS					
Site	Pottsville	Mauch Chunk	Greenbriar	Pocono	Hampshire	Ernest Dekalb	Penn Meckesville	Belmont Meckesville	Dekalb	Calvin	VSL[1] Dekalb
100	31.6	33.7	7.8	2.8	24.1	38.1	21.1	8.2	4.6	24.6	3.4
110	32.0	34.1	7.8	2.9	23.2	37.2	21.2	9.0	4.9	24.2	3.4
120	0	35.7	8.0	2.8	20.0	29.1	22.2	9.2	4.6	21.4	2.5
210	0	4.9	10.8	4.7	79.6	0	4.9	10.8	4.7	79.6	0
220	0	0	9.5	8.8	81.7	0	0	10.6	7.0	82.4	0
230	0	0	0	0	100.0	0	0	0	0	100.0	0
241	0	28.2	35.4	10.6	25.8	0	16.8	24.7	8.3	50.2	0
251	0	11.8	26.4	12.4	49.4	0	1.6	23.4	12.0	63.0	0
261	0	25.4	31.0	11.2	32.4	0	28.2	35.4	10.6	25.8	0
271	0	78.5	20.9	0.6	0	0	71.9	28.1	0	0	0
242	0	1.8	6.3	3.4	88.5	0	1.8	6.3	3.4	88.5	0
252	0	0	1.1	3.0	95.9	0	0	0	2.5	97.5	0
262	0	10.1	32.9	12.6	44.4	0	10.1	32.9	12.6	44.4	0
272	0	0	0	0	100.0	0	0	0	0	100.0	0
130	39.4	41.4	8.6	2.5	8.1	50.5	24.9	8.5	4.2	7.5	4.4
131	0	2.8	18.3	16.8	62.1	0	1.8	15.7	35.9	46.5	0

---

[1] Very stony land.

	GEOLOGY					SOILS					
Site	Pottsville	Mauch Chunk	Greenbriar	Pocono	Hampshire	Ernest Dekalb	Penn Meckesville	Belmont Meckesville	Dekalb	Calvin	VSL[1] Dekalb
140	42.1	43.9	8.2	2.0	3.8	54.0	26.2	8.0	3.6	3.5	4.7
310	0	26.3	34.3	13.0	26.4	0	27.0	34.4	13.4	25.2	0
320	0	37.6	46.8	9.5	6.1	0	38.4	45.4	10.4	5.8	0
330	0	65.1	34.9	0	0	0	69.1	30.9	0	0	0
340	0	84.4	15.6	0	0	0	89.2	10.8	0	0	0
350	0	100.0	0	0	0	0	100.0	0	0	0	0
150	43.8	44.7	7.2	1.6	2.7	56.2	26.0	7.0	3.3	2.6	4.9
151	0	35.2	29.1	9.2	28.5	0	38.5	27.1	8.6	25.8	0
152	0	49.0	37.3	3.0	10.7	0	49.0	33.7	3.0	10.7	0
160	46.3	45.5	6.1	1.2	0.9	59.5	25.6	6.0	2.9	0.8	5.2
161	0	65.6	26.6	4.0	3.8	0.4	65.3	26.2	3.7	4.4	0
170	49.0	44.5	4.9	1.0	0.6	62.9	23.6	4.7	2.8	0.5	5.5
180	56.2	42.5	1.3	0	0	70.7	19.6	1.3	2.3	0	6.1
181	0	87.0	13.0	0	0	0	88.4	11.6	0	0	0
182	14.6	81.2	4.2	0	0	38.7	50.6	4.0	6.0	0	0.7
183	13.1	86.8	0.1	0	0	31.8	62.2	0.9	5.1	0	0

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[1] Very stony land.

	GEOLOGY					SOILS					
Site	Pottsville	Mauch Chunk	Greenbriar	Pocono	Hampshire	Ernest Dekalb	Penn Meckesville	Belmont Meckesville	Dekalb	Calvin	VSL[1] Dekalb
190	64.1	35.9	0	0	0	79.8	11.0	0	1.9	0	7.3
191	48.1	51.9	0	0	0	61.3	38.7	0	0	0	0
200	70.1	29.9	0	0	0	86.0	4.1	0	1.8	0	8.1
410	69.6	30.4	0	0	0	85.3	2.6	0	3.6	0	8.5
420	79.9	20.1	0	0	0	81.3	0	0	5.7	0	13.0
430	90.4	9.6	0	0	0	97.3	0	0	0	0	2.7
440	100.0	0	0	0	0	65.0	0	0	9.3	0	25.7
450	100.0	0	0	0	0	61.0	0	0	7.2	0	31.8
500	70.9	29.1	0	0	0	87.3	4.6	0	0.4	0	7.7
501	78.4	21.6	0	0	0	86.4	2.9	0	1.8	0	8.9
510	82.3	17.7	0	0	0	93.7	1.6	0	0	0	4.7
511	80.5	19.5	0	0	0	91.2	0	0	0	0	8.8
520	73.1	26.9	0	0	0	91.4	0.8	0	0	0	7.8
530	90.6	9.4	0	0	0	88.0	0	0	0	0	12.0
531	75.4	24.6	0	0	0	96.9	0	0	0	0	3.1
540	62.9	37.1	0	0	0	98.7	0	0	0	0	1.3

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[1] Very stony land.

sites on the watershed. The number of discharge observations ranged from a minimum of five per site to a maximum of 27 at the watershed mouth.

Additional data available for the project included mean daily discharge from two nearby watersheds, Taylor Run (1,310 ha) and Watershed No. 4 (35 ha) of the Fernow Experimental Forest for the 1974, 1975 and 1976 water years, and precipitation quality measurements from four rain gages near the Little Black Fork Basin (Figure 3). Precipitation samples at most of the gages were collected from April 1974 through March 1976 and analyzed for the same water quality parameters as the surface runoff.

WATER QUALITY OF THE STUDY AREA

In this section, the inorganic chemical water quality of the study area is discussed with specific reference given to the relationships between stream chemistry and soil and geologic complexes. The section is divided into three parts: cluster analysis, interpretation of the mean water quality data and seasonal variations in stream chemistry.

Cluster Analysis

Cluster analysis is a classification method used to determine similarity between objects. It was applied to the Little Black Fork data to identify those sites with similar chemical water quality and to determine in an objective manner if relationships exist between the particular soil and rock complexes exposed and chemical water quality. The cluster program used in this study was developed by Veldman (1967).

In order to interpret the results of the cluster analysis correctly, it is important that the data transformations and program assumptions are clearly understood. First, since the purpose of the cluster analysis was to identify those sites with similar water quality, a single set of data was needed to characterize the water quality at each site. Therefore, average values for each parameter at each site were used in the analysis. It should be noted that the data were neither flow nor time weighted. Examination of the data set showed little variation in the average values when calculated by simple arithmetic averaging versus weighted averages. The mean values, standard deviations and range of the water quality parameters for each site are given in Appendix A.

Second, the variation in each parameter within the data set for each site was scaled to an equal range. For instance, mean sulfate concentrations varied from 6.3 to 12.6 mg/l. They were scaled from 0 to 100, such that 6.3 mg/l was equated to 0 and 12.6 mg/l equated to 100. The intermediate sulfate concentrations were then distributed within this range. The scaling procedure forces the variation in each parameter to be equal. It should be noted that mean hydrogen ion activities were used instead of mean pH. This was done to assure that all parameters would be scaled in an equal manner. pH is a logarithmic transformation of hydrogen ion activity, or a scaling from 0 to 14, while hydrogen ion activity represents the effective hydrogen ion concentration.

Third, each parameter was given equal weighting in the calculation of similarity. This caused differences in potassium concentrations to be just as important as differences in conductivity measurements when grouping the water quality of a site.

The cluster dendrogram for the mean water quality data is shown in Figure 6. This diagram illustrates the similarity between sites. Results from the cluster analysis indicate that water quality at sites draining similar soil and geologic types is also similar. The water quality of sites draining the Pottsville group and its associated soils showed

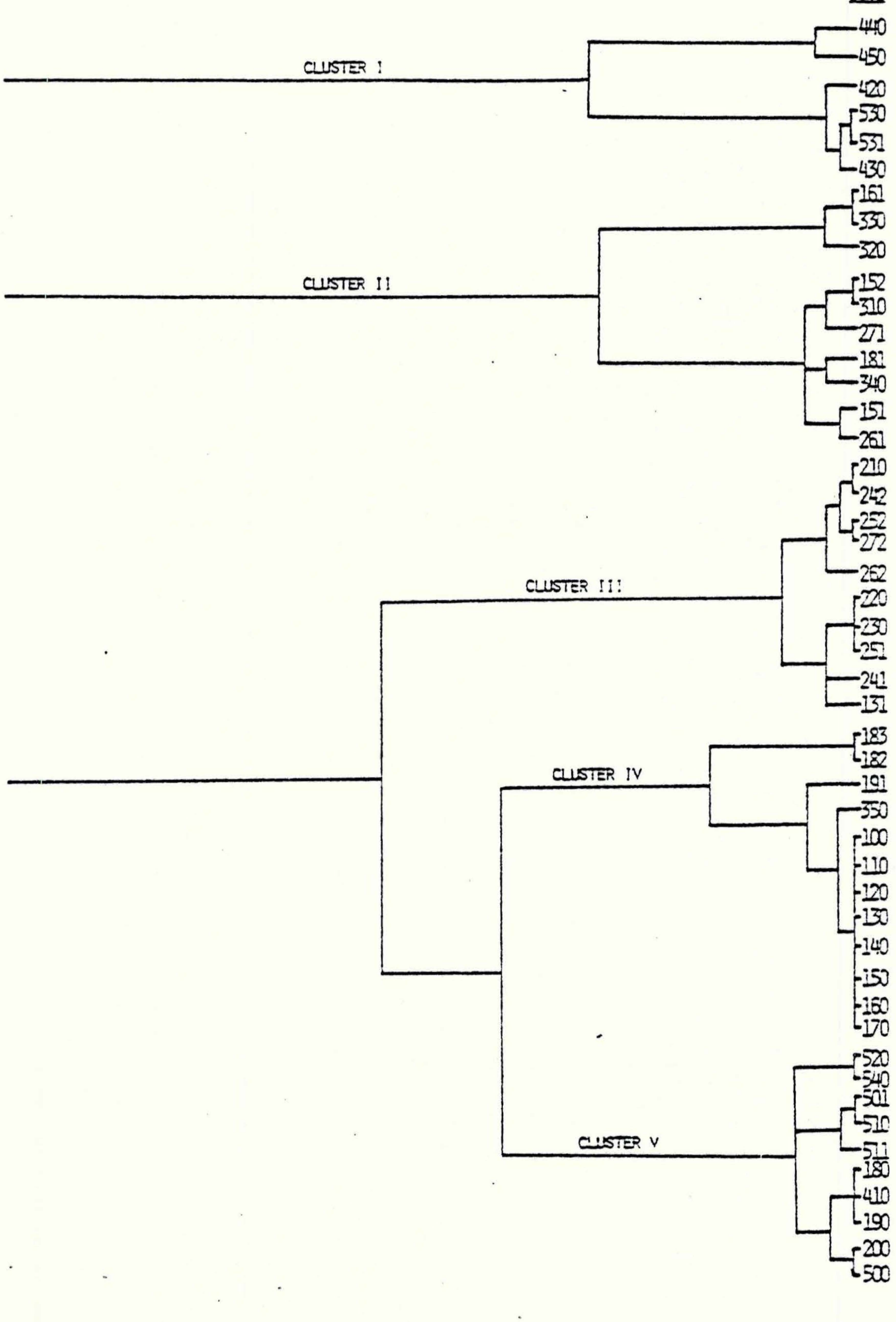

SITE
CLUSTER I
440
450
420
530
531
430
CLUSTER II
161
330
320
152
310
271
181
340
151
261
CLUSTER III
210
242
252
272
262
220
230
251
241
131
CLUSTER IV
183
182
191
350
100
110
120
130
140
150
160
170
CLUSTER V
520
540
501
510
511
180
410
190
200
500

Figure 6. Cluster dendrogram for the mean water quality of sites on the Little Black Fork basin.

similarity (Cluster I). Water quality of sites draining large areas of the carbonaceous Greenbriar group also appear to be similar (Cluster II). In addition, sites from the Hampshire formation are similar to each other (Cluster III), sites on the main stem draining similar proportions of the various soil and rock complexes, along with sites draining predominantly the Mauch Chunk group are similar to each other (Cluster IV) and sites draining both the Mauch Chunk and Pottsville group (Cluster V) are clustered together.

The relationship between stream chemistry and soil and geologic complexes for each of the cluster groupings is discussed in detail in the following section.

Water Quality Relationships

Precipitation

Table 2 summarizes the precipitation data for the study area. In general, precipitation is acidic with low concentrations of dissolved solids. The mean pH of 4.25 is substantially lower than the pH of 5.65 which results when pure water is in equilibrium with carbon dioxide at standard temperature and pressure. This low pH, coupled with the relatively high sulfate concentrations, suggests that sulfuric acid has formed in the precipitation. The sulfur for the sulfuric acid formation is possibly derived from sulfur dioxide emissions in the industrialized Ohio River Valley which lies upwind of the study area. The low pH of the precipitation may enhance chemical weathering of the rock types on the watershed, especially the carbonate types.

Table 2. Mean ($\overline{X}$) and standard deviation (s) of the precipitation water quality.

Site	Specific Conduct. (μmhos/cm)	Hydrogen Ion Activity (pH) (Mg/l)	Acidity (mg/l) as $CaCO_3$)	Alkalinity (mg/l as $CaCO_3$)	Iron (mg/l)	Sulfate (mg/l)	Nitrate Nitrogen (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Potassium (mg/l)
Stillwell											
$\overline{X}$	28.8	8.7×10^{-5} (4.06)	6.1	1.2	0.087	5.5	0.75	0.65	0.20	1.16	0.32
s	8.4	2.6×10^{-4}	2.2	1.6	0.026	2.6	0.37	0.42	0.32	1.83	0.24
Bickel Nob											
$\overline{X}$	35.1	5.4×10^{-5} (4.27)	8.2	0.3	0.061	5.3	0.62	0.52	0.11	0.73	0.32
s	30.2	2.7×10^{-5}	4.1	0.7	0.018	1.6	0.47	0.27	0.06	0.98	0.27
Clifton Run											
$\overline{X}$	33.0	5.0×10^{-5} (4.30)	6.0	0.7	0.087	5.1	0.76	0.64	0.16	0.38	0.37
s	14.6	3.5×10^{-5}	1.6	1.5	0.032	2.4	0.49	0.38	0.10	0.25	0.17
Fernow Site B											
$\overline{X}$	36.0	5.2×10^{-4} (4.28)	9.7	1.2	0.087	5.6	1.98	0.76	0.21	0.86	0.42
s	17.6	4.0×10^{-5}	5.1	3.2	0.038	2.4	1.74	0.52	0.30	1.51	0.36
Fernow Site D											
$\overline{X}$	41.0	4.5×10^{-5} (4.35)	9.6	1.3	0.071	5.1	1.95	0.70	0.14	0.86	0.67
s	57.4	2.7×10^{-5}	5.9	4.0	0.031	2.3	2.06	0.74	0.13	1.46	0.77
All Sites Combined											
$\overline{X}$	35.8	5.6×10^{-5} (4.25)	8.8	1.1	0.079	5.3	1.59	0.68	0.17	0.83	0.46

The concentration of other ions in the precipitation is relatively low, as suggested by the low mean specific conductance (35.8 μmhos/cm), and probably has little effect on runoff quality.

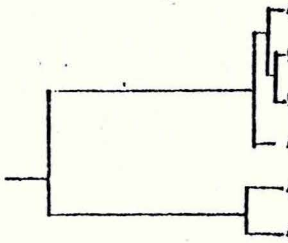
Cluster I (Pottsville Group)

The geologic, soil and stream chemistry data for sites in Cluster I is summarized in Table 3. The sites in this Cluster (420, 430, 440, 450, 530 and 531) are located in the upper reaches of the watershed and drain predominantly from the Pottsville geologic group and the associated Ernest and Dekalb soil series (Figure 7). Sites 440 and 450 drain exclusively from the Pottsville rock group and derived soil while sites 420, 430, 530 and 531 drain a small portion of the Mauch Chunk rock type. The Mauch Chunk group at these sites, however, is overlain by Ernest and Dekalb colluvium derived from the Pottsville group above.

Stream chemistry for sites in this cluster is typified by a low pH ranging from 4.0 to 5.0, substantial acidity and very low alkalinity. Sulfate, as in the precipitation, is the major anion in solution. Cation concentrations, with the exception of iron, are similar to those in precipitation samples, reflecting the slow weathering rate of the Pottsville sandstones.

Due to the isolated occurrence of pyrite in the Pottsville group, the chemistry of water draining from this rock type can vary substantially. The oxidation of pyrite (FeS_2) releases hydrogen ions which lowers the pH and raises the acidity. Excess sulfate and iron ions are also

Table 3. Percent of geologic and soil types drained and mean water quality data for sites in Cluster I.

Cluster Dendrogram	Site	Percent Geologic Type					Percent Soil Type						Spec Cond (µmhos/cm)	pH (su)	Acd (mg/l) as $CaCO_3$	Alk (mg/l) as $CaCO_3$	Fe (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)
		Pottsville	Mauch Chunk	Greenbriar	Pocono	Hampshire	Ern-Dek	Penn-Meck	Bel-Meck	Dekalb	Calvin	VSL-Dekalb											
	420	80	20	0	0	0	81	0	0	6	0	13	38	4.52	7.7	0.6	0.11	8.1	0.97	1.95	0.51	0.47	0.39
	530	91	9	0	0	0	88	0	0	0	0	12	38	4.33	9.2	0.0	0.08	7.8	0.88	1.05	0.31	0.51	0.32
	531	91	9	0	0	0	97	0	0	0	0	3	37	4.41	8.2	0.2	0.09	7.8	0.90	1.32	0.40	0.46	0.36
	430	90	10	0	0	0	97	0	0	0	0	3	48	4.36	11.3	0.0	0.09	9.3	1.11	1.59	0.51	0.50	0.47
	440	100	0	0	0	0	65	0	0	9	0	26	49	4.23	10.4	0.0	0.16	9.6	1.20	1.65	0.44	0.41	0.44
	450	100	0	0	0	0	61	0	0	7	0	32	56	4.07	12.3	0.0	0.22	10.2	1.20	1.34	0.36	0.44	0.39

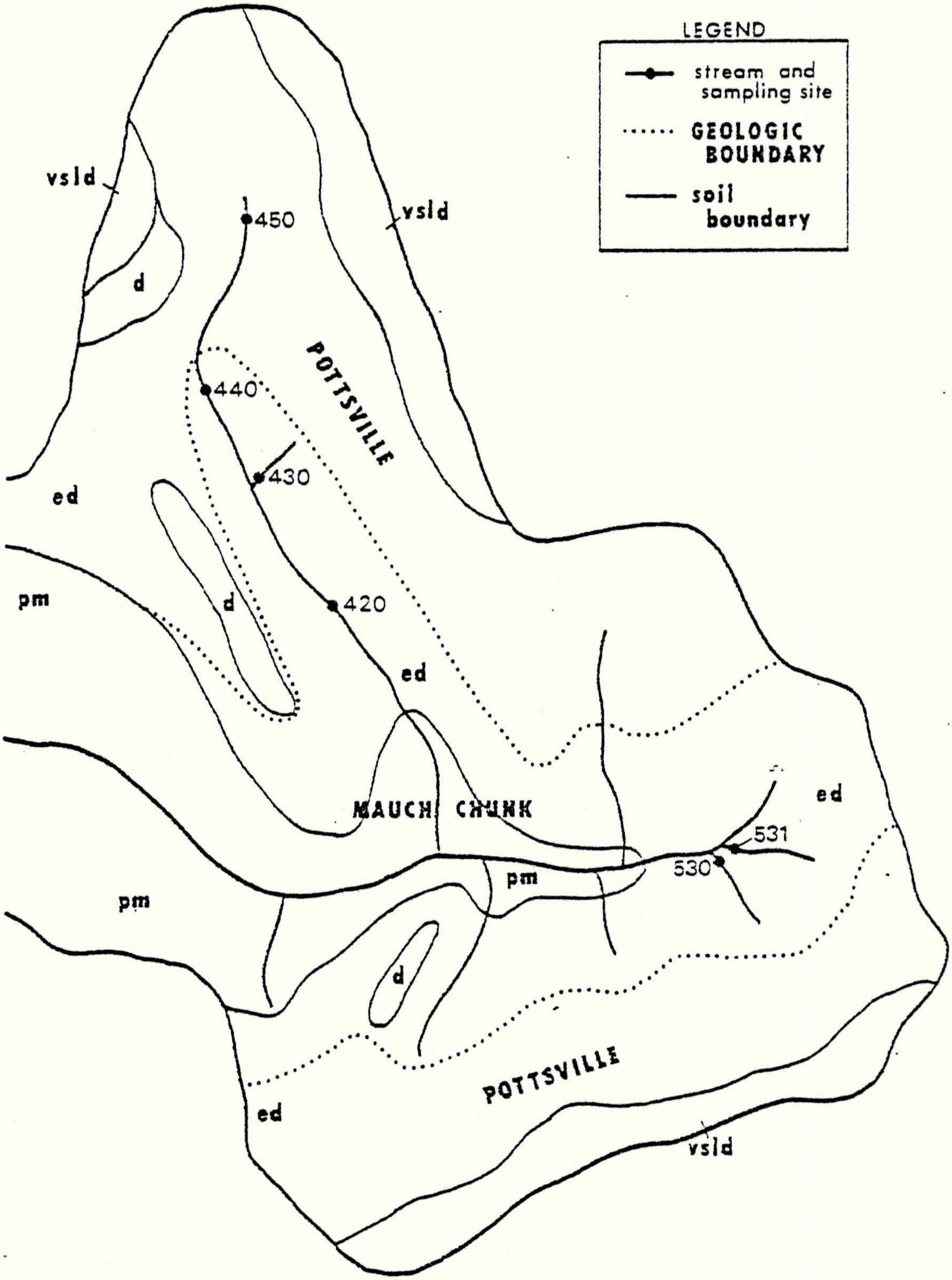

LEGEND
stream and sampling site
GEOLOGIC BOUNDARY
soil boundary
vsld
vsld
vsld
d
d
d
ed
ed
ed
ed
pm
pm
pm
POTTSVILLE
POTTSVILLE
MAUCH CHUNK
450
440
430
420
530
531

Figure 7. Location of the sites in Cluster I in relation to the geologic groups and soil associations. Soil associations are denoted by vsld (Very Stony Land-Dekalb), ed (Ernest-Dekalb), d (Dekalb) and pm (Penn-Meckesville).

produced and result in an increase in specific conductance. The effect of pyrite oxidation is readily observed in the cluster of sites 440 and 450. These sites, while similar to each other, differ from the other sites in Cluster I. The pH at sites 440 and 450 is noticeably lower than the pH at the other sites while sulfate, iron, acidity and specific conductance concentrations are substantially increased. This indicates that the greatest amount of pyrite oxidation is taking place above these sites and, in particular, above site 450 where the lowest pH and greatest sulfate concentrations occur.

The cluster of sites 420, 530, 531 and 430 does not exhibit the marked effect of pyrite oxidation. Acidity, sulfate and iron concentrations are lower while pH is generally higher than at sites 440 and 450. Each of these sites has similar water quality and, in addition, drain similar proportions of soil and geologic material.

The degree of pyrite oxidation in the Pottsville group appears to coincide with the proportion of Very Stony Land - Dekalb soil type exposed. For example, as water moves downstream from site 450 to 420, the concentrations of acidity, sulfate and iron decrease while pH increases. This change in stream chemistry corresponds readily with the decreasing percent of Very Stony Land - Dekalb soil from 32 percent at site 450, to 26 percent at site 440, to 12 percent at site 420. In addition, the two sites draining the largest proportion of this soil type, sites 450 and 440, exhibit the strongest effects of pyrite oxidation. The Very Stony Land - Dekalb soil is shallow and rocky and might readily expose the pyritic materials present in the Pottsville rock type.

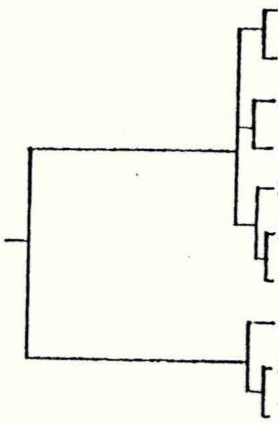
Cluster II (Greenbriar Group)

The proportional areal coverage by the various geologic groups and soil series along with the average water quality data for each site in Cluster II are summarized in Table 4. The sites grouped in this cluster (151, 152, 161, 181, 261, 271, 310, 320, 330 and 340) drain a substantial proportion of the carbonate Greenbriar group and its related Belmont-Meckesville soil association. Each of these sites is located either on the Greenbriar Group or downstream from it (Figure 8).

The readily weathered Greenbriar carbonates appear to have a major effect upon stream chemistry of the sites in this cluster (Table 4). Calcium, magnesium and alkalinity concentrations as well as pH and specific conductance levels are greatly increased over those associated with precipitation or the other soil and geologic complexes exposed on the watershed. The large rise in each of these parameters is directly related to the rapid weathering of the calcium and magnesium carbonates. Waters in this cluster also have increased sulfate concentrations.

The large change in stream chemistry brought about by this rock type is readily apparent from the data of the 300 series drainage. At site 340 the stream has just entered the Greenbriar Group and shows moderate effects with a slightly basic pH and a conductivity of 155 µmhos/cm.

Table 4. Percent of geologic and soil types drained and average water quality data for sites in Cluster II.

Cluster Dendrogram	Site	Percent Geologic Type					Percent Soil Type						Spec Cond (umhos/cm)	pH (su)	Acd (mg/l) as $CaCO_3$	Alk (mg/l) as $CaCO_3$	Fe (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)
		Pottsville	Mauch Chunk	Greenbriar	Pocono	Hampshire	Ern-Dek	Penn-Meck	Bel-Meck	Dekalb	Calvin	VSL-Dekalb											
	261	0	17	33	13	37	0	28	35	11	26	0	139	7.42	2.8	52.7	0.07	10.1	1.28	19.06	1.54	1.21	0.89
	151	0	35	27	9	29	0	39	27	9	26	0	152	7.57	2.3	55.9	0.07	11.6	1.16	21.06	1.81	1.30	0.99
	340	0	84	16	0	0	0	89	11	0	0	0	155	7.56	3.8	61.6	0.08	10.3	1.09	18.09	1.32	0.93	0.52
	181	0	87	13	0	0	0	88	12	0	0	0	132	7.33	2.0	43.1	0.06	10.0	1.46	18.45	1.44	1.77	0.67
	271	0	61	38	1	0	0	72	28	0	0	0	216	7.77	3.0	90.1	0.08	10.5	1.69	26.57	1.97	1.15	0.82
	310	0	26	34	13	26	0	27	34	13	25	0	206	7.79	2.4	87.2	0.08	11.4	1.12	28.10	1.94	1.01	0.77
	152	0	56	34	7	14	0	49	34	7	11	0	180	7.86	1.9	72.8	0.07	11.4	1.15	24.58	1.76	0.88	0.66
	320	0	38	47	9	6	0	38	45	10	6	0	263	7.99	2.0	111.7	0.10	11.5	1.23	32.77	2.14	0.82	0.61
	330	0	65	35	0	0	0	69	31	0	0	0	303	8.08	1.8	135.7	0.07	12.0	1.41	31.99	2.30	0.82	0.51
	161	0	66	27	4	4	0	65	26	4	4	0	312	7.96	2.2	141.1	0.07	12.6	1.49	33.76	2.39	1.02	0.70

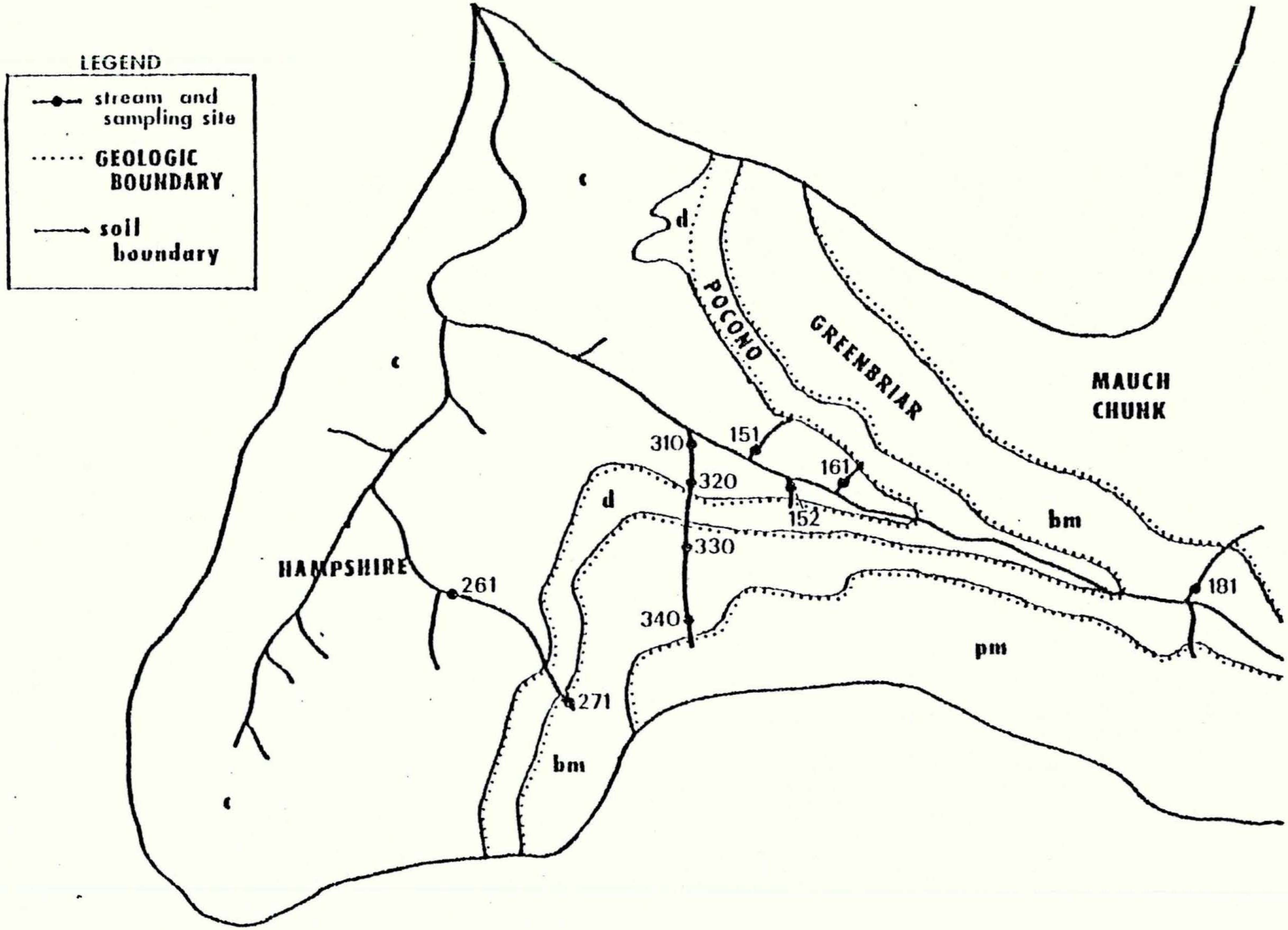

LEGEND
stream and sampling site
GEOLOGIC BOUNDARY
soil boundary
c
c
c
d
d
POCONO
GREENBRIAR
MAUCH CHUNK
HAMPSHIRE
bm
bm
pm
310
151
161
320
152
330
340
261
271
181

Figure 8. Location of the sites in Cluster II in relation to the geologic groups and soil associations. Soil associations are denoted by pm (Penn-Meckesville), bm (Belmont-Meckesville), d (Dekalb) and c (Calvin).

By the time the stream has passed the short distance to site 330, just below the Greenbriar rock group, specific conductance, calcium, magnesium, sulfate, alkalinity and pH levels are greatly increased. Stream chemistry remains virtually unchanged as the water flows away from the Greenbriar group, further indicating the controlling nature of this rock type on stream chemistry.

The water quality of sites within Cluster II are partitioned into two separate subclusters. The first subcluster consists of sites 161, 320 and 330, which exhibit the greatest effect of the carbonate rock type. Calcium, magnesium, alkalinity, sulfate, pH and specific conductance concentrations are higher at these sites than anywhere else on the watershed. These sites drain almost exclusively from Greenbriar and Mauch Chunk geologic and soil complexes.

The other subcluster, containing sites 151, 152, 181, 261, 271 and 310 exhibits characteristics common to the Greenbriar group but not to the same degree that is observed at sites 161, 320 and 330. These sites have lower concentrations of calcium, magnesium, sulfate, alkalinity, specific conductance and pH and, in general, drain a smaller proportion of the Greenbriar complex.

In addition, several other site groupings occur within this subcluster. Sites 181 and 340, which drain the smallest proportion of the carbonate Greenbriar complex, have the lowest calcium, magnesium, and alkalinity concentrations of any sites within Cluster II. Sites 151 and 261 cluster together and drain similar proportions of the various soil and geologic complexes, including increased amounts of the Hampshire formation. Stream chemistry at these sites is very similar to that at sites 181 and 340, except for increased potassium concentrations which are possibly a result of the micaceous sandstones in the Hampshire rock type. In addition, potassium concentrations are also increased at sites 271 and 310, again due to the Hampshire influence.

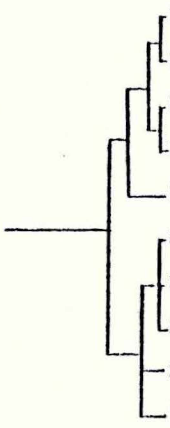
Cluster III (Hampshire Formation)

The average water quality and the geology and soils data are summarized in Table 5 for sites in Cluster III. All sites in this cluster drain predominantly from the Hampshire formation and the associated Calvin soil series. Each of the sites is located in the lower portion of the watershed and, with the exception of site 131, are in the 200 series drainage (Figure 9).

Stream chemistry in this cluster is typified by a slightly acidic to neutral pH, relatively low specific conductance and dissolved ion concentrations and substantially higher potassium concentrations than those sites associated with other soil and rock groups of the watershed. The low dissolved solids concentrations reflect the slow weathering rate of the Hampshire shales and sandstones. The increase in potassium concentration is probably a result of the micaceous sandstones present in the formation.

The stream chemistry of sites within this cluster is very similar as indicated by the short horizontal connecting lines between sites.

Table 5. Percent of geologic and soil types drained and average water quality data for sites in Cluster III.

Cluster Dendrogram	Site	Percent Geologic Type					Percent Soil Type						Spec Cond (μmhos/cm)	pH (su)	Acd (mg/l) as $CaCO_3$	Alk (mg/l) as $CaCO_3$	Fe (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)
		Pottsville	Mauch Chunk	Greenbriar	Pocono	Hampshire	Ern-Dek	Penn-Meck	Bel-Meck	Dekalb	Calvin	VSL-Dekalb											
	210	0	3	8	5	85	0	5	11	5	80	0	43	6.94	2.2	10.4	0.06	7.8	0.65	4.19	0.82	0.88	0.97
	242	0	1	3	2	94	0	2	6	3	89	0	31	6.54	2.5	5.4	0.08	6.7	0.61	2.14	0.70	0.78	0.94
	252	0	0	1	3	96	0	0	0	3	97	0	25	6.17	3.2	3.8	0.10	6.8	0.48	1.45	0.65	0.92	0.85
	272	0	0	0	0	100	0	0	0	0	100	0	22	6.18	2.9	3.9	0.12	6.9	0.82	2.11	0.57	0.87	0.80
	262	0	6	23	7	65	0	10	33	13	44	0	48	6.82	12.1	12.1	0.08	8.0	0.72	4.81	0.94	0.85	0.94
	220	0	0	10	9	82	0	11	0	7	82	0	30	6.30	2.7	4.2	0.06	7.5	0.60	1.87	0.71	0.89	0.87
	230	0	0	0	0	100	0	0	0	0	100	0	32	6.20	2.4	5.1	0.06	8.0	0.71	2.29	0.81	0.89	0.82
	251	0	12	26	12	50	0	2	23	12	63	0	35	6.26	2.8	4.7	0.07	8.1	0.84	1.93	0.88	1.05	0.95
	241	0	10	21	10	59	0	17	25	8	50	0	78	7.09	2.6	25.9	0.07	8.5	0.91	9.91	1.08	1.10	0.86
	131	0	3	18	17	62	0	2	16	36	47	0	32	6.45	2.5	3.8	0.08	8.7	0.53	1.75	0.81	1.27	0.78

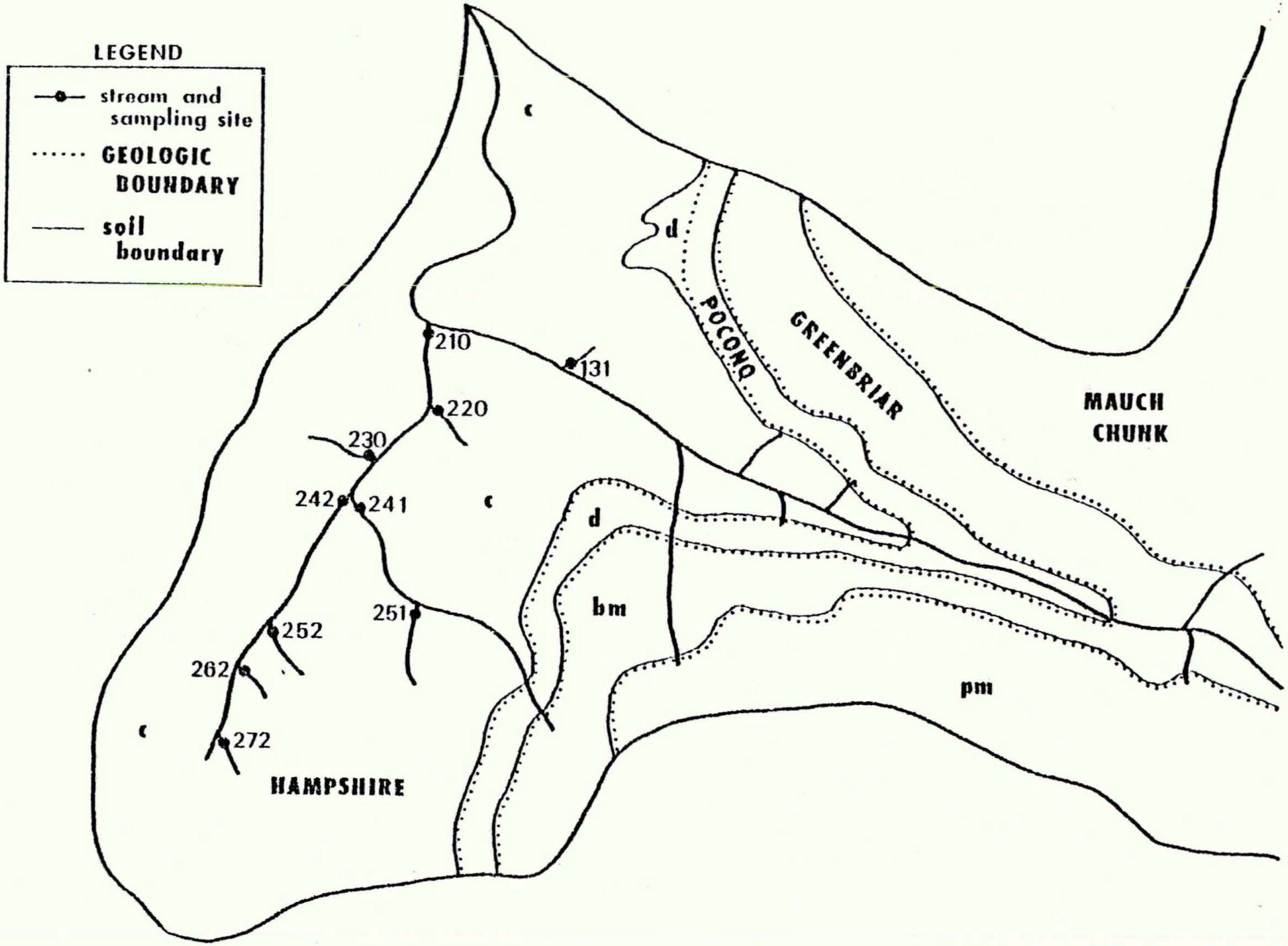

LEGEND
stream and sampling site
GEOLOGIC BOUNDARY
soil boundary
c
d
POCONO
GREENBRIAR
MAUCH CHUNK
210
131
220
230
242
241
c
d
bm
251
252
262
272
pm
c
HAMPSHIRE

Figure 9. Location of the sites in Cluster III in relation to the geologic groups and soil associations. Soil associations are denoted by pm (Penn-Meckesville), bm (Belmont-Meckesville), d (Dekalb) and c (Chemung).

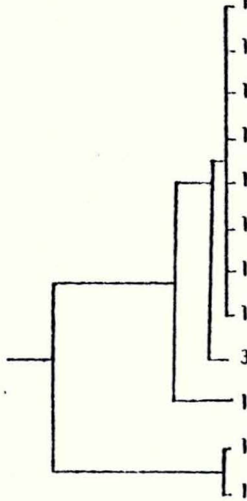
The water quality of sites 131, 220, 230, 242, 251, 252 and 272 is influenced predominantly by the Hampshire formation as evidenced by the relatively low specific conductance, calcium and magnesium concentrations.

Sites 210, 241 and 262 appear to be influenced by the Greenbriar group. These sites have increased specific conductance, pH, alkalinity, calcium and magnesium concentrations corresponding to the increased proportions of the carbonate soil and rock type in their drainage areas. Sites 251 and 131 also drain a substantial proportion of the Greenbriar group; however, stream chemistry at these sites shows no indication of higher calcium, magnesium, alkalinity, specific conductance, or pH concentrations. These results suggest that very little, if any, Greenbriar drainage occurs at these sites and that possibly an error in the delineation of the soil and geologic maps has been made.

Cluster IV (Mauch Chunk Group and Mainstream Sites)

The geologic, soil and average water chemistry data for sites in Cluster IV are listed in Table 6. The sites in this cluster are grouped into two subclusters, those predominantly draining from the Mauch Chunk group (182, 183, 191 and 350) and those located along the main stem of the Little Black Fork (100, 110, 120, 130, 140, 150, 160 and 170) draining a mixture of geologic types (Figure 10). The sites along the main stem drain almost identical proportions of the various geologic groups and soil series exposed on the watershed.

Table 6. Percent of geologic and soil types drained and average water quality data for sites in Cluster IV.



Cluster Dendrogram	Site	Percent Geologic Type: Pottsville	Mauch Cnunk	Greenbriar	Pocono	Hampshire	Percent Soil Type: Ern-Dek	Penn-Meck	Bel-Meck	Dekalb	Calvin	VSL-Dekalb	Spec Cond (µmhos/cm)	pH (su)	Acd (mg/l) as $CaCO_3$	Alk (mg/l) as $CaCO_3$	Fe (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)
	100	32	34	8	3	24	38	21	8	5	25	3	64	7.17	2.3	17.0	0.06	8.5	1.00	8.59	0.91	0.91	0.72
	110	32	34	8	3	23	38	21	9	5	24	3	64	7.23	2.1	17.5	0.06	8.6	0.86	8.70	0.92	0.88	0.56
	120	34	36	8	3	20	39	22	9	5	21	4	64	7.23	2.1	17.9	0.06	8.3	0.88	8.73	0.91	0.87	0.63
	130	39	41	9	3	8	51	25	8	4	8	4	67	7.20	2.1	17.8	0.06	8.0	0.93	8.87	0.91	0.93	0.56
	140	42	44	8	2	4	54	26	8	4	4	5	67	7.22	2.1	18.7	0.07	8.2	0.97	8.91	0.90	0.89	0.51
	150	44	45	7	2	3	56	26	7	3	3	5	66	7.35	2.2	18.3	0.07	8.7	1.01	8.47	0.88	0.87	0.53
	160	46	46	6	1	1	60	26	6	3	1	5	63	7.27	2.1	17.7	0.07	8.2	1.02	8.26	0.87	0.82	0.48
	170	49	45	5	1	1	63	24	5	3	1	6	63	7.35	2.2	15.8	0.06	7.9	1.05	7.80	0.85	0.82	0.52
	350	0	100	0	0	0	0	100	0	0	0	0	77	7.39	2.3	22.2	0.09	8.9	0.79	9.47	1.04	1.03	0.52
	191	48	52	0	0	0	61	39	0	0	0	0	40	6.68	2.4	6.7	0.07	6.6	1.35	4.06	0.72	0.89	0.61
	182	15	81	4	0	0	39	51	4	6	0	1	77	7.11	2.1	17.9	0.07	11.7	1.20	9.08	1.19	1.21	0.55
	183	13	87	0	0	0	32	62	1	5	0	0	71	7.12	2.1	15.9	0.08	11.7	1.20	7.48	1.24	1.29	0.57

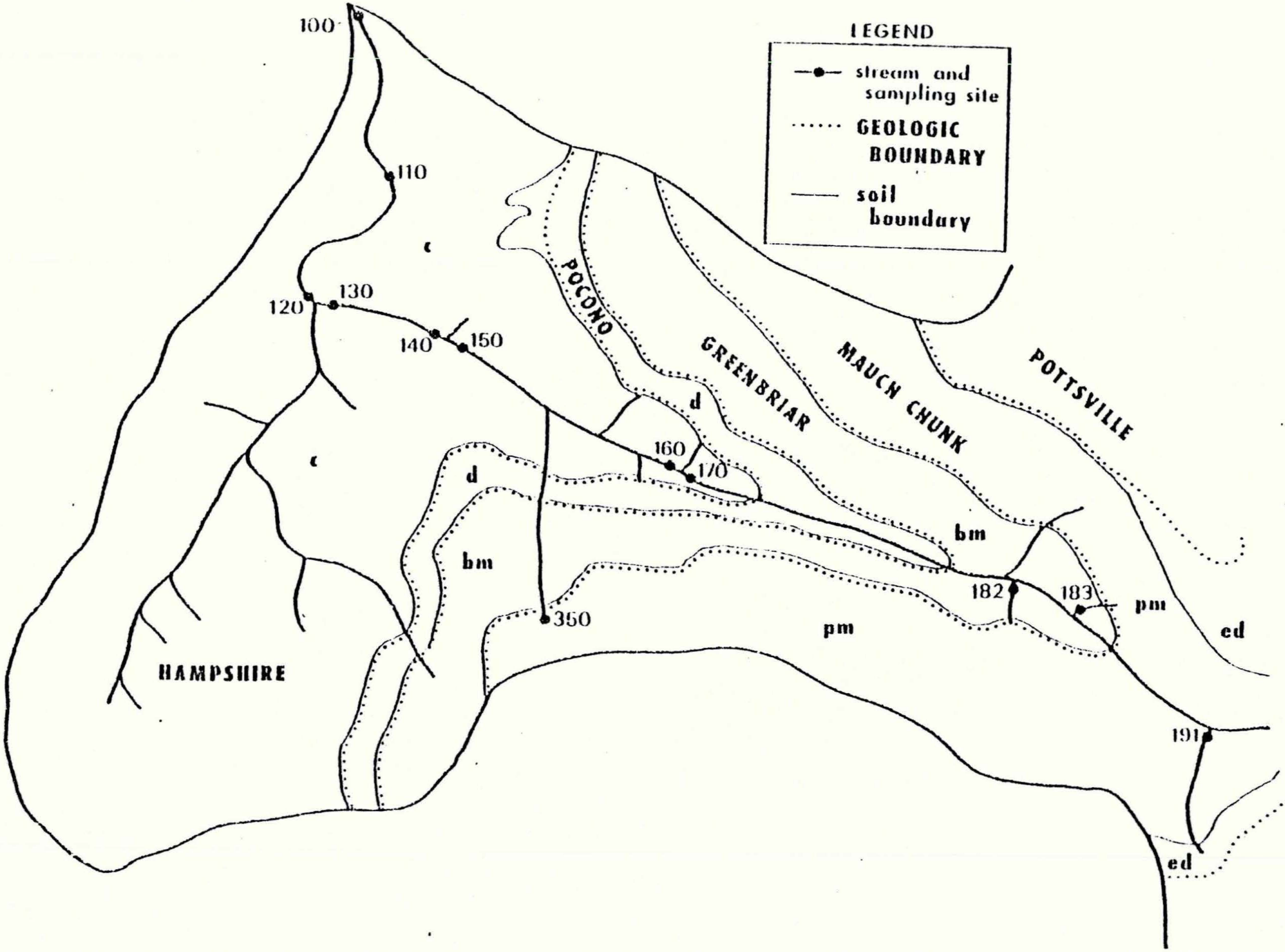

LEGEND
stream and sampling site
GEOLOGIC BOUNDARY
soil boundary
100
110
120
130
140
150
160
170
182
183
191
350
c
c
d
d
bm
bm
pm
pm
ed
ed
POCONO
GREENBRIAR
MAUCH CHUNK
POTTSVILLE
HAMPSHIRE

Figure 10. Location of the sites in Cluster IV in relation to the geologic groups and soil associations. Soil associations are denoted by pm (Penn-Meckesville), bm (Belmont-Meckesville), d (Dekalb), c (Calvin) and ed (Ernest-Dekalb).

The stream chemistry of sites in Cluster IV is intermediate in relation to that of sites associated with other soil and rock complexes on the watershed. Average specific conductance generally varies from 63 to 77 µmhos/cm, mean pH is slightly basic and alkalinity exceeds acidity. The water at these sites is not as acidic as water associated with the Pottsville complex, nor is it as basic as water draining the Greenbriar carbonates. Dissolved ion concentrations and specific conductance are higher than in water from the Hampshire and Pottsville groups and lower than in water from the Greenbriar group.

Sites 182, 183, 191 and 350 of this cluster drain large proportions of the Mauch Chunk group and the associated Penn and Meckesville soil types. Site 350 drains exclusively from Mauch Chunk material. The mean specific conductance at this site is 77 µmhos/cm, average pH is 7.39 and alkalinity, calcium and magnesium concentrations are all increased. This conductance level suggests that Mauch Chunk shales weather more readily than the Pottsville or Hampshire rock groups but not as easily as the Greenbriar group. The increased pH, alkalinity, calcium and magnesium concentrations indicate that a substantial amount of carbonate material is weathered from the Mauch Chunk group.

Sites 191, 182 and 183 drain not only from the Mauch Chunk but also from the Pottsville soil and rock complexes. As expected, due to the acidic and resistant nature of the Pottsville material, pH, specific conductance, alkalinity, calcium and magnesium are all lower than that at site 350, in an amount roughly proportional to the percent of Pottsville complex drained. Site 191, which drains the greatest percentage of the Pottsville complex, has the lowest pH, alkalinity, specific conductance and dissolved ion concentrations of these three sites.

Each of the sites along the main stem has practically identical water quality. Stream chemistry at these sites (100, 110, 120, 130, 140, 150, 160 and 170) exhibits the combined influence of the many soil and rock complexes exposed on the watershed. The dominant effect upon water quality at these sites is from the complexes containing carbonates (Mauch Chunk and the Greenbriar). pH is slightly basic and alkalinity, calcium and magnesium concentrations are higher, indicating carbonate dissolution.

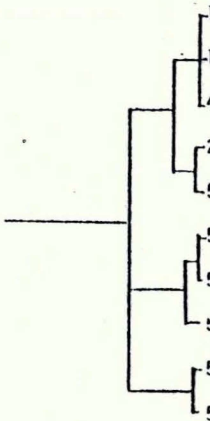
The effect of the Hampshire formation is apparent in the lower sites (100, 110, 120 and 130). As the percent of Hampshire complex increases at these sites, potassium concentrations also rise.

Cluster V (Mauch Chunk and Pottsville Groups)

The geologic, soil and average stream quality data for sites in Cluster V are summarized in Table 7. Each site present in this cluster is situated below the Pottsville and Mauch Chunk complexes (Figure 11). These sites (180, 190, 200, 410, 500, 501, 510, 520 and 540) drain predominantly from the acidic Pottsville complex, and to a lesser extent, from the Mauch Chunk group and its associated soils.

The mean water quality at these sites reflects the acidic characteristics of the Pottsville group; however, due to the carbonaceous nature of the Mauch Chunk complex the acid characteristics

Table 7. Percent of geologic and soil types drainaed and average water quality data for sites in Cluster V.

		Percent Geologic Type					Percent Soil Type																
Cluster Dendrogram	Site	Pottsville	Mauch Chunk	Greenbrier	Pocono	Hampshire	Ern-Dek	Penn-Meck	Bel-Meck	Dekalb	Calbin	VSL-Dekalb	Spec Cond (μmhos/cm)	(su)	Acd (mg/l) as $CaCO_3$	Alk (mg/l) as $CaCO_3$	Fe (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)
	180	56	43	1	0	0	71	20	1	2	0	6	42	6.99	2.1	7.0	0.08	8.2	1.00	4.55	0.67	0.78	0.43
	190	64	36	0	0	0	80	11	0	2	0	8	34	6.40	2.4	4.5	0.08	7.8	0.97	3.58	0.61	0.76	0.46
	410	70	30	0	0	0	85	3	0	4	0	9	32	5.81	3.1	3.2	0.08	7.7	0.99	2.94	0.65	0.70	0.44
	200	70	30	0	0	0	86	4	0	2	0	8	29	5.43	3.0	2.5	0.10	7.3	0.90	2.76	0.58	0.68	0.43
	500	71	29	0	0	0	87	5	0	1	0	8	27	5.14	3.7	1.9	0.11	7.2	0.80	2.03	0.50	0.61	0.38
	501	78	22	0	0	0	86	3	0	2	0	9	30	5.55	2.8	2.4	0.06	6.6	1.20	2.51	0.59	0.54	0.39
	510	82	18	0	0	0	93	0	0	0	2	5	31	4.89	5.3	1.3	0.05	6.6	1.11	1.83	0.55	0.44	0.39
	511	80	20	0	0	0	91	0	0	0	0	9	26	5.41	3.1	2.0	0.07	6.9	0.87	1.94	0.58	0.47	0.45
	520	73	27	0	0	0	91	1	0	0	0	8	29	4.61	6.3	0.7	0.08	7.5	0.76	1.37	0.37	0.52	0.34
	540	73	27	0	0	0	99	0	0	0	0	1	22	4.83	4.8	1.3	0.09	6.3	0.73	1.12	0.35	0.51	0.41

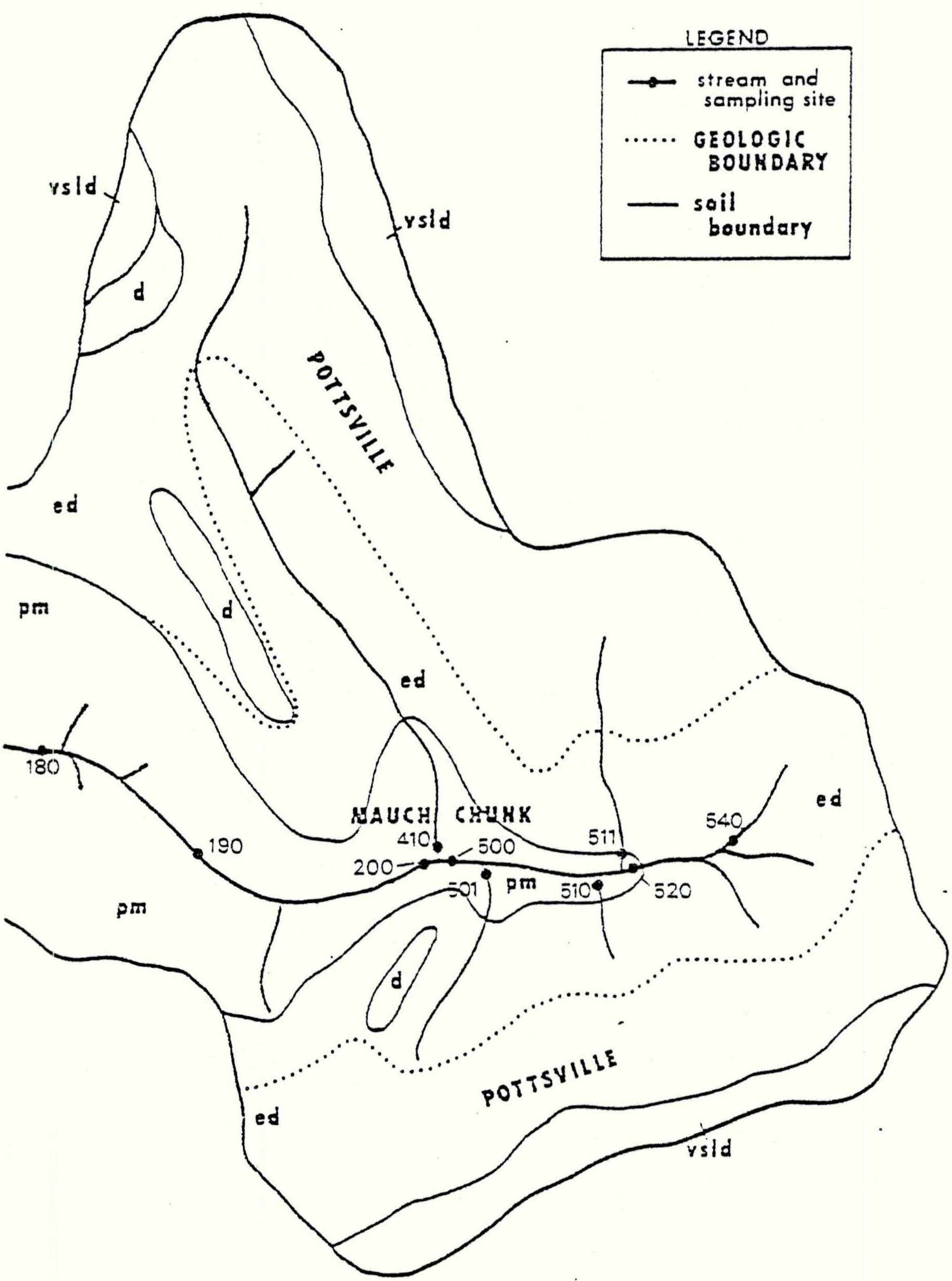

LEGEND
stream and sampling site
GEOLOGIC BOUNDARY
soil boundary
vsld
vsld
d
POTTSVILLE
ed
pm
d
ed
180
190
MAUCH CHUNK
410
500
200
501
pm
511
540
ed
510
520
pm
d
POTTSVILLE
ed
vsld

Figure 11. Location of the sites in Cluster V in relation to the geologic groups and soil associations. Soil associations are denoted by vsld (Very Stony Land-Dekalb), ed (Ernest-Dekalb), d (Dekalb) and pm (Penn-Meckesville).

are buffered and not as pronounced in waters draining only the Pottsville soil and rock complexes. Alkalinity and pH are both increased while acidity is decreased as compared to sites in the Pottsville cluster (Cluster I).

The slight differences in stream chemistry within this cluster can be related to the areal coverage of Mauch Chunk complexes drained. Generally, the larger the proportion of the Mauch Chunk group drained, the higher the pH, alkalinity and ion concentrations. Site 180 drains the greatest amount of Mauch Chunk complex and has the highest pH, alkalinity and ion concentrations of the sites in this cluster. Sites 510, 511, 520 and 540 drain the smallest proportion of the Mauch Chunk complex and generally have the most acid waters. The remainder of the sites in this cluster (190, 410, 200, 500 and 501) have stream chemistry reflecting intermediate proportions of Mauch Chunk soil and rock complexes.

The influence of the Mauch Chunk group appears to coincide with the boundary of the Ernest-Dekalb soil association (Pottsville derived) and the Penn-Meckesville soil association (Mauch Chunk derived), not with the boundary between the Pottsville and Mauch Chunk rock groups. Four sites in the Pottsville cluster, 420, 530, 531 and 430, drain substantial proportions of Mauch Chunk rock type. The rock type is covered by acidic Ernest-Dekalb colluvium. These four sites show little, if any, Mauch Chunk influence. However, in Cluster V, at sites draining similar proportions of Pottsville and Mauch Chunk rock types but located below the Ernest-Dekalb and Penn-Meckesville soil boundary, the influence of the Mauch Chunk group is apparent. Acidity is decreased while alkalinity and pH are increased.

Pocono and Chemung Groups

Two other geologic groups, the Pocono and Chemung, are present on the watershed. These rock types, in particular the Chemung, are exposed on a very small portion of the basin and in such a manner that their influence upon stream chemistry is difficult to ascertain.

The Pocono group and its associated Dekalb soil series are exposed on about 32 ha or 2.6 percent of the watershed surface. The structure and mineral composition of this rock group are very similar to that of the acidic Pottsville group. It is estimated that runoff from the Pocono group has similar characteristics to that from the Pottsville rock type, i.e., low specific conductance, low pH, substantial acidity concentrations and little or no alkalinity.

The Chemung group is exposed on about one ha near the watershed mouth, less than one-tenth of a percent of the total watershed area. Due to its minimal exposure, this rock type has practically no influence on stream chemistry of the Little Black Fork Basin.

Overall, the geologic groups and soil series exposed on the watershed influence stream chemistry in many different ways. A summary of the influence of each soil and geologic complex is given in Table 8.

Seasonal Variations in Stream Chemistry

The water quality data for each site were averaged over several seasons to determine if temporal variations in stream chemistry exist. Averages were computed for winter (January-February), spring (March-April), summer (May-September), fall (October-December) and the recharge

Table 8. Summary of the influence of each soil and geologic complex upon stream chemistry.

Soil and Geologic Complex	Composition	Relative Rate of Weathering	General Influence Upon Stream Chemistry
Pottsville	Acidic Sandstones	Slow	low pH (4.0-5.0), low specific conductance (38-56 μmhos/cm), substantial acidity (7.7-12.3 mg/l as $CaCO_3$), alkalinity near 0 mg/l as $CaCO_3$.
Greenbriar	Calcium and Magnesium Carbonates	Rapid	basic pH (> 8.1), high specific conductance (> 300 μmhos/cm), high alkalinity (> 140 mg/l as $CaCO_3$), increased calcium (> 33 mg/l) and magnesium (> 2.4 mg/l).
Hampshire	Shales and Micaceous Sandstones	Slow	Slightly acidic pH (6.0-6.5, low specific conductance (20-30 μmhos/cm), increased potassium concentrations.
Mauch Chunk	Shales	Moderate	Slightly basic pH, intermediate calcium, magnesium, alkalinity and specific conductance levels.
Pocono	Acidic Sandstones	Slow	Acid pH (est.), low specific conductance (est.), more acidity than alkalinity (est.).

and depletion periods. The duration of the recharge and depletion periods was estimated from mean monthly discharge records of the adjacent Taylor Run Basin during the study period (Figure 12). Recharge was assumed to occur from November through March with depletion lasting from April to September.

Cluster analysis was applied to the average water quality data for each of the six periods. The resultant cluster dendrograms were nearly identical, indicating that the same general relationships between stream chemistry and the soil and rock complexes exist throughout the year.

Most of the variation in the water quality data appears to be independent of season. However, several minor variations were noted between the different seasonal averages. The following is a discussion of temporal trends in stream chemistry for each of the main cluster groups identified in Figure 6 and for the mouth of the watershed (Site 100).

Cluster I (Pottsville Group)

In general, sulfate, iron and acidity concentrations increased during the spring months (March and April) at sites in Cluster I, indicating a greater degree of pyrite oxidation during this period. For example, at site 440 average sulfate concentrations increase from 10.1 mg/l in the winter to 10.g mg/l in the spring, average iron concentrations rise from 0.12 to 0.19 mg/l and mean acidity levels increase from 10.1 to 12.8 mg/l as $CaCO_3$ while pH decreases slightly.

Another trend noted at these sites is the increased concentration of dissolved ions, with the exception of iron, sulfate and potassium,

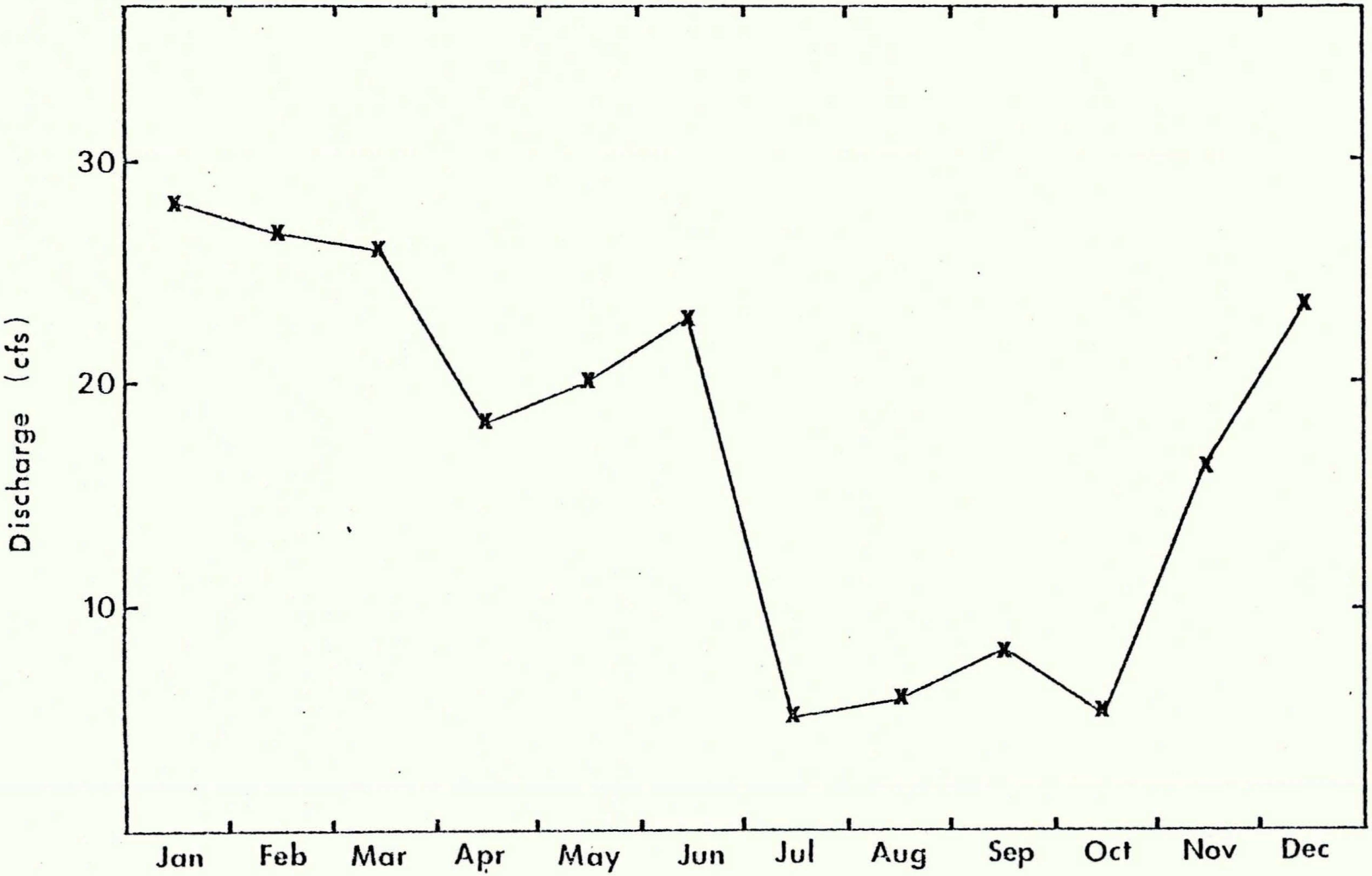


Figure 12. Mean monthly discharge for Taylor Run basin, October 1973-April 1976.

during the summer and fall. This response is possibly due to concentration of dissolved ion mass resulting from increased evapotranspiration during the summer and early fall.

While the concentration of most dissolved ions increases during the summer months, potassium concentrations decrease. For instance, at site 450 the mean spring potassium concentration is 0.42 mg/l while the summer average is 0.29 mg/l. This phenomenon was also noted during the Hubbard Brook study in New Hampshire, where it was attributed to the increased utilization of potassium ions by plants during the growing season (Likens, *et.al*., 1977).

Cluster II (Greenbriar Group)

The stream chemistry of sites grouped in Cluster II also exhibits slight seasonal trends. Specific conductance, alkalinity and the concentration of dissolved ions are generally higher during the summer and fall months than during the rest of the year. This is exemplified by the mean water quality data at site 310. Specific conductance for the spring is 198 μmhos/cm while in the summer months it is 229 μmhos/cm, calcium concentrations increase from 26.30 to 27.12 mg/l, magnesium levels rise from 1.66 to 2.14 mg/l, sodium concentrations increase from 0.83 to 1.13 mg/l and alkalinity increases from 78.3 to 100.8 mg/l as $CaCO_3$. These increases may again be due to greater evapotranspiration during the summer and fall resulting in a concentration of dissolved solids mass.

Cluster III (Hampshire Formation)

Sites in the Hampshire formation also have increased concentrations of dissolved ions in the summer and fall. Potassium, acidity, alkalinity, calcium and magnesium concentrations, while all low, are highest in the period of May through December. In general, little change in pH, iron concentration or specific conductance occurs at these sites.

Cluster IV (Mainstream Sites and Mauch Chunk Group)

The mainstream sites located in Cluster IV exhibit little seasonal change in water quality. Specific conductance and dissolved ion concentrations are slightly higher in late summer and fall while potassium levels are slightly lower during the May through September period.

Stream chemistry at sites draining predominantly from the Mauch Chunk varies substantially. During the summer and fall the concentration of dissolved ions increases in a similar manner to that from waters draining from the Greenbriar, Pottsville and Hampshire soil and rock complexes. At site 182, draining predominantly from the Mauch Chunk complex, average specific conductance for the spring months is 72 µmhos/cm while for May through September it is 118 µmhos/cm. Mean alkalinity increases during this period from 14.4 to 39.8 mg/l as $CaCO_3$, average calcium concentrations rise from 7.92 to 16.54 mg/l and mean magnesium concentrations increase from 1.02 to 1.59 mg/l. Potassium ion concentrations in these waters generally decrease slightly during the summer months.

Cluster V (Mauch Chunk and Pottsville Groups)

Sites in this cluster, which drain from the Pottsville and Mauch Chunk groups, strongly reflect the temporal differences in dissolved ion concentrations associated with the Mauch Chunk group. In the winter and spring, when the concentrations of dissolved material associated with the Mauch Chunk complex are least, dominance of the Pottsville group is noted: acidity rises, while pH, alkalinity, calcium and magnesium concentrations decrease. In the summer and fall the Mauch Chunk complex has a greater effect on stream chemistry. The concentrations of dissolved ions along with alkalinity and pH are increased, while acidity is generally decreased. This change in water quality can be seen at site 190. Average pH for the fall is 6.73 while during the winter it is 6.15. In addition, average alkalinity concentrations decrease from 5.3 to 4.6 mg/l as $CaCO_3$, mean calcium concentrations drop from 4.16 to 3.45 mg/l and mean sodium concentration decreases from 0.88 to 0.60 mg/l.

Watershed Mouth (Site 100)

Seasonal averages of water quality at the mouth of the watershed are summarized in Table 9. In general, there is little change in the water quality data between seasons. Conductivity remains relatively low, ranging between 63 and 68 µmhos/cm, pH is slightly basic while acidity remains virtually constant. Alkalinity shows a slight increase during the summer along with a corresponding increase in calcium. Potassium concentrations increase in summer and fall while the other constituents remain relatively unchanged.

Table 9. Seasonal averages of water quality at site 100.

Season	SC (µmhos/ cm)	pH (su)	Acidity (mg/l as $CaCO_3$)	Alkalinity (mg/l as $CaCO_3$)	Fe (mg/l)	SO_4 (mg/l)	NO_3-N (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	K (mg/l)
Winter (Jan-Feb)	68	7.16	2.3	15.8	0.06	8.8	0.90	7.79	0.88	0.78	0.49
Spring (Mar-Apr)	65	7.10	2.4	15.5	0.06	9.4	1.03	7.70	0.87	0.74	0.54
Summer (June-Sept)	64	7.22	2.3	18.8	0.06	7.5	1.15	9.62	0.93	0.97	0.71
Fall (Oct-Dec)	63	7.19	2.1	14.8	0.07	8.9	0.85	8.31	0.93	1.04	1.03

In summary, the seasonal trends discussed in this section are general in their nature. They correspond to variations in concentrations only, not mass. Although most of the variation in the data appears to occur independently of season, a few trends were discernible. The concentrations of most constituents are greatest during summer and fall. This is probably due to the concentration of mass resulting from evapotranspiration. Elements which are readily absorbed by woody plants, such as potassium, generally decrease during the growing season. The Pottsville complex appears to have its greatest influence during the winter and spring as evidenced by the relatively high concentrations of the products of pyrite oxidation.

PREDICTION OF SPECIFIC CONDUCTANCE AND HYDROGEN ION ACTIVITY

Function Objective

The specific objectives of the functions developed in this chapter was to predict the baseline specific conductance and pH of surface waters draining the Little Black Fork Basin as related to the soil and geologic complexes exposed. To enhance their utility by field-based hydrologists, several constraints were placed on the development of the functions. First, input data were restricted to basic climatic, hydrologic, soil and geologic information. Second, the functions were to yield predictions of reasonable accuracy, within five percent error for conductivity and half a standard unit for pH. Third, the method of development should have application to other waters within the Monongahela National Forest.

Data Evaluation

Correlation of Parameters

Prior to the development of the prediction functions, it was necessary to determine if specific conductance and pH were independent of each other and, in turn, how they related to the other water quality parameters. If specific conductance and pH were highly correlated, i.e., dependent upon each other, there would be no need to develop separate functions for both parameters. In essence, both functions would then be predicting the same thing. Furthermore, if an additional parameter, such as alkalinity, were highly correlated with specific conductance or pH, it could be estimated with a minor modification of the respective function.

Table 10 presents the correlation coefficients (r) of the various parameters. The coefficients indicate that specific conductance and hydrogen ion activity (pH) are not highly correlated and, therefore, may be predicted independently. In addition, alkalinity, calcium and magnesium are highly related to specific conductance, indicating that a predictive function for specific conductance could easily be modified to simulate these parameters as could a pH function be modified to simulate acidity.

Function Conceptualization

Variations in water quality associated with fluctuations in streamflow have been documented in many studies (Lane, 1975; Hall, 1970; Toler, 1965; Hendrickson and Krieger, 1964; and Langbein and Dawdy, 1964). Generally, as discharge increases and the proportion of groundwater flow is reduced, a dilution effect occurs and dissolved solids concentrations decrease. Inversely, as discharge decreases and the proportion of groundwater flow increases, dissolved solids concentrations usually increase.

Table 10. Correlation coefficients (r) of the water quality parameters.

	Spec. Cond.	Hyd. Ion Act.	Acd.	Alk.	Fe	SO_4	NO_3-N	Ca	Mg	Na	K
Specific Conductance	1.00	-0.21	-0.23	0.99	-0.11	0.81	0.70	0.98	0.95	0.38	0.16
Hydrogen Ion Activity	-0.21	1.00	0.97	-0.29	0.70	-0.02	0.03	-0.34	-0.44	-0.64	-0.47
Acidity	-0.23	0.97	1.00	-0.31	0.62	-0.07	0.00	-0.36	-0.46	-0.67	-0.47
Alkalinity	0.99	-0.29	-0.31	1.00	-0.15	0.77	0.64	0.98	0.95	0.40	0.21
Iron	-0.11	0.70	0.62	-0.15	1.00	0.08	-0.07	-0.19	-0.24	-0.33	-0.09
Sulfate	0.81	-0.02	-0.07	0.77	0.08	1.00	0.65	0.79	0.82	0.50	0.18
Nitrate-Nitrogen	0.70	0.03	0.00	0.64	-0.07	0.65	1.00	0.68	0.63	0.21	0.16
Calcium	0.98	-0.34	-0.36	0.98	-0.19	0.79	0.68	1.00	0.97	0.47	0.22
Magnesium	0.95	-0.44	-0.46	0.95	-0.24	0.82	0.63	0.97	1.00	0.62	0.38
Sodium	0.38	-0.64	-0.67	0.40	-0.33	0.50	0.21	0.47	0.62	1.00	0.66
Potassium	0.16	-0.47	-0.47	0.21	-0.09	0.18	-0.16	0.22	0.38	0.66	1.00

A relationship between stream chemistry and discharge was intially assumed to exist for surface waters of the Little Black Fork Basin. To account for this relationship, a modification of the Ponce and Hawkins (1978) mass-balance function was proposed to simulate specific conductance and pH at different levels of streamflow. Since the water quality of the basin appeared to correspond with the percent of the various geologic and soil complexes drained, an area weighting modification to the mass-balance function was proposed for use on the basis of mixed soil and geologic composition. The proposed models took the forms:

$$\hat{SC} = K\Sigma_i \frac{A_i SC_i}{q_i} \qquad [3]$$

and

$$\hat{pH} = -\log K\Sigma_i \frac{A_i H_i}{q_i} \qquad [4]$$

where $\hat{SC}$ is the simulated specific conductance, SC_i is a dissolved solids loading factor for the i'th soil and geologic complex, A_i is the percent of the total basin area occupied by complex i, q_i is the discharge per unit area from complex i, $\hat{pH}$ is the simulated pH, H_i is an excess hydrogen ion loading factor for complex i and K is a proportionality constant.

Discharge simulation. In order to develop the mass-balance models, a complete set of discharge and water quality data was needed. This required that the missing discharge values be simulated.

An initial attempt to simulate discharge utilized by the Kentucky Watershed Model, a Fortran adaptation of the Stanford Watershed Model IV (Striffler, 1973). This model, which simulates daily streamflow, uses a moisture accounting procedure to route water inputs from precipitation or melting snowpack through the various components of the hydrologic cycle. Data requirements include hourly precipitation, daily maximum and minimum temperatures and daily, 10 day, or monthly mean evapotranspiration. Numerous coefficients that control the rates of snow melt infiltration, overland flow, interflow, soil water depletion and groundwater storage must be estimated. If daily discharge is known, an optimization routine may be used which provides an estimate of many of these coefficients.

The Kentucky Watershed Model was first applied to watershed number 4 of the Fernow Experimental Forest, for which detailed precipitation, temperature and streamflow data were available. This watershed is located 11 km north-northwest of the Little Black Fork watershed and is about 35 ha in size. Model coefficients were estimated with the optimization routine and measured streamflow from this basin. The model was then applied to the mouth of the Little Black Fork watershed (Site 100). The model results deviated substantially from the infrequent discharge observations at Site 100.

A second attempt to estimate streamflow was based on a regression correlation between observed discharge of the Taylor Run watershed and the streamflow measurements at Site 100. The Taylor Run basin is located about 10 km southeast of the study watershed and is similar in size (1,310 ha) and watershed characteristics to the Little Black Fork basin (1,230 ha). A notable exception is that only Pottsville, Mauch Chunk and Greenbriar soil and geologic complexes are exposed on the Taylor Run basin. A good linear correlation ($r^2 = 0.99$) existed between the 16 streamflow observations at site 100 and the corresponding discharge measurements from the Taylor Run basin. Simulated streamflow from this linear correlation was substantially closer to the observed discharge at site 100 than was simulated streamflow from the Kentucky Watershed Model (Table 11).

In addition, good correlations existed between discharge at site 100 and streamflow at numerous other sites on the Little Black Fork basin. The discharge regression equations for these sites along with coefficients of variation and the number of observations used to develop the equations are listed in Table 12. It should be noted that these equations were developed from a limited number of data points, thereby restricting their validity. However, they do allow a reasonable estimate of missing discharge data to be made for numerous sites on the study watershed.

The runoff data synthesized from these equations were used to examine the relationships between conductivity or pH and discharge at the various sites. Examples of these relationships are shown in Figure 13 through 16. It was readily apparent from these rating curves that conductivity and pH respond independently of discharge. As a result,

Table 11. Comparison of simulated discharge from the Kentucky Watershed Model and the Taylor Run regression for site 100.

Date	Observed Discharge (cfs)	Taylor Fork[1] Regression (cfs)	Kentucky Watershed Model (cfs)
1/4/75	10.2	8.1	12.5
3/13/75	41.6	37.9	34.4
4/25/75	66.2	67.8	78.0
5/22/75	7.3	7.8	5.5
7/22/75	2.8	3.0	1.1
8/21/75	6.6	6.0	19.7
9/16/75	1.1	1.6	1.6
10/21/75	13.8	7.8	1.1
11/11/75	2.7	1.9	0.1
1/13/76	9.2	13.0	13.3
2/20/76	16.9	15.5	18.0
3/10/76	3.7	4.5	4.9
3/25/76	14.4	13.8	8.8
4/7/76	15.7	14.7	6.3
4/20/76	2.7	3.7	0.9
5/4/76	12.1	10.5	1.2
5/19/76	17.5	7.8	2.3

[1] $Q_{100} = 0.56 + 0.83\ Q_{\text{Taylor Run}}$

$R^2 = 0.99$

$n = 16$

Table 12. Regression equations for the simulation of Little Black Fork streamflow.

Equation by Site[1]	Coefficient of Variation (r^2)	Number of Observations (n)
$Q_{100} = 0.56 + 0.83\ Q_{\text{Taylor Run}}$	0.99	16
$Q_{130} = 1.26 + 0.99\ Q_{100}$	0.96	14
$Q_{150} = -1.34 + 0.82\ Q_{100}$	0.97	14
$Q_{200} = 0.46\ Q_{100}^{(1.03)}$	0.91	8
$Q_{410} = -0.12 + 0.18\ Q_{100}$	0.93	13
$Q_{500} = 0.11\ Q_{100}^{(1.26)}$	0.83	13

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[1] Subscript denotes site number.

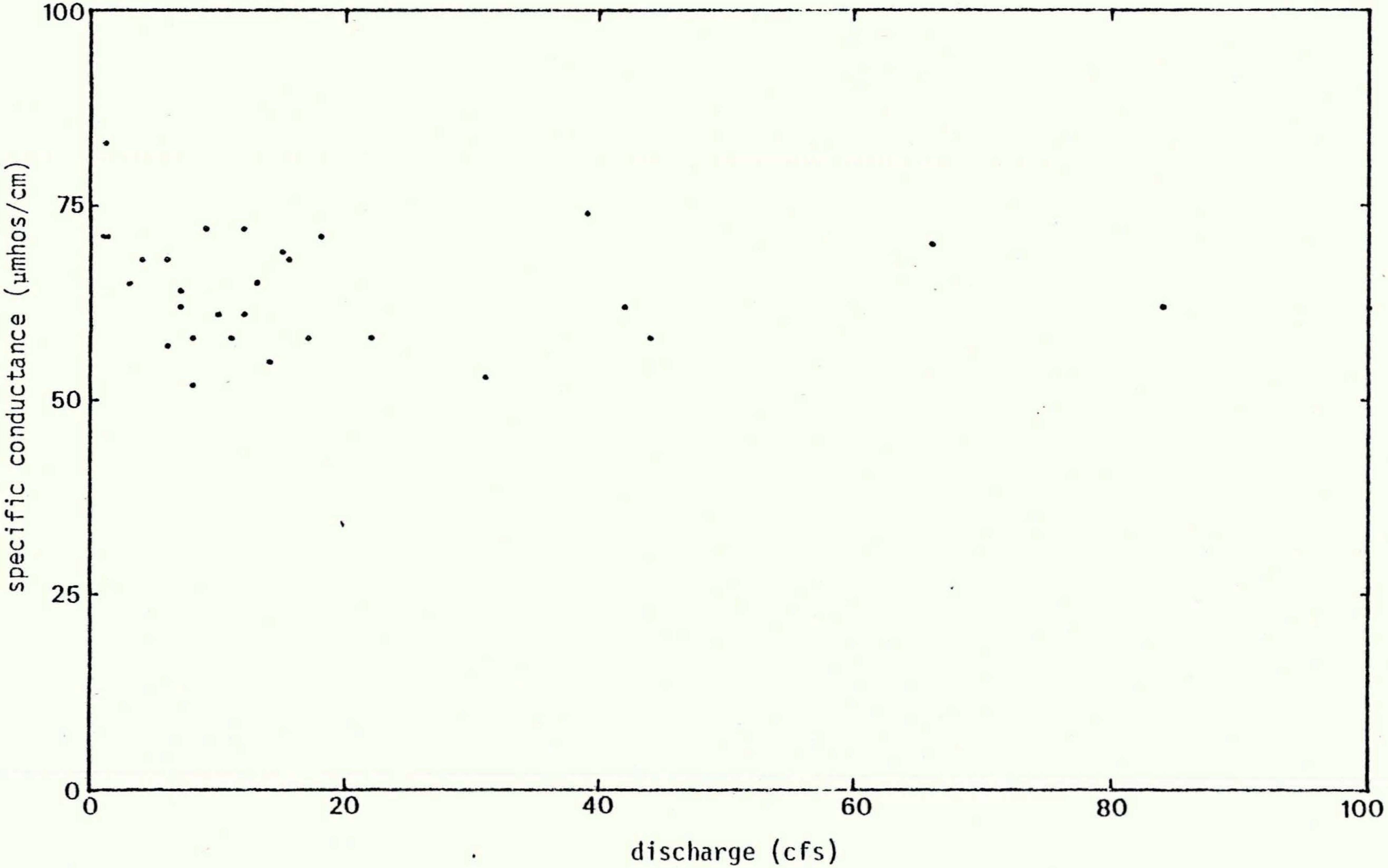

Figure 13. Specific conductance versus discharge, site 100.

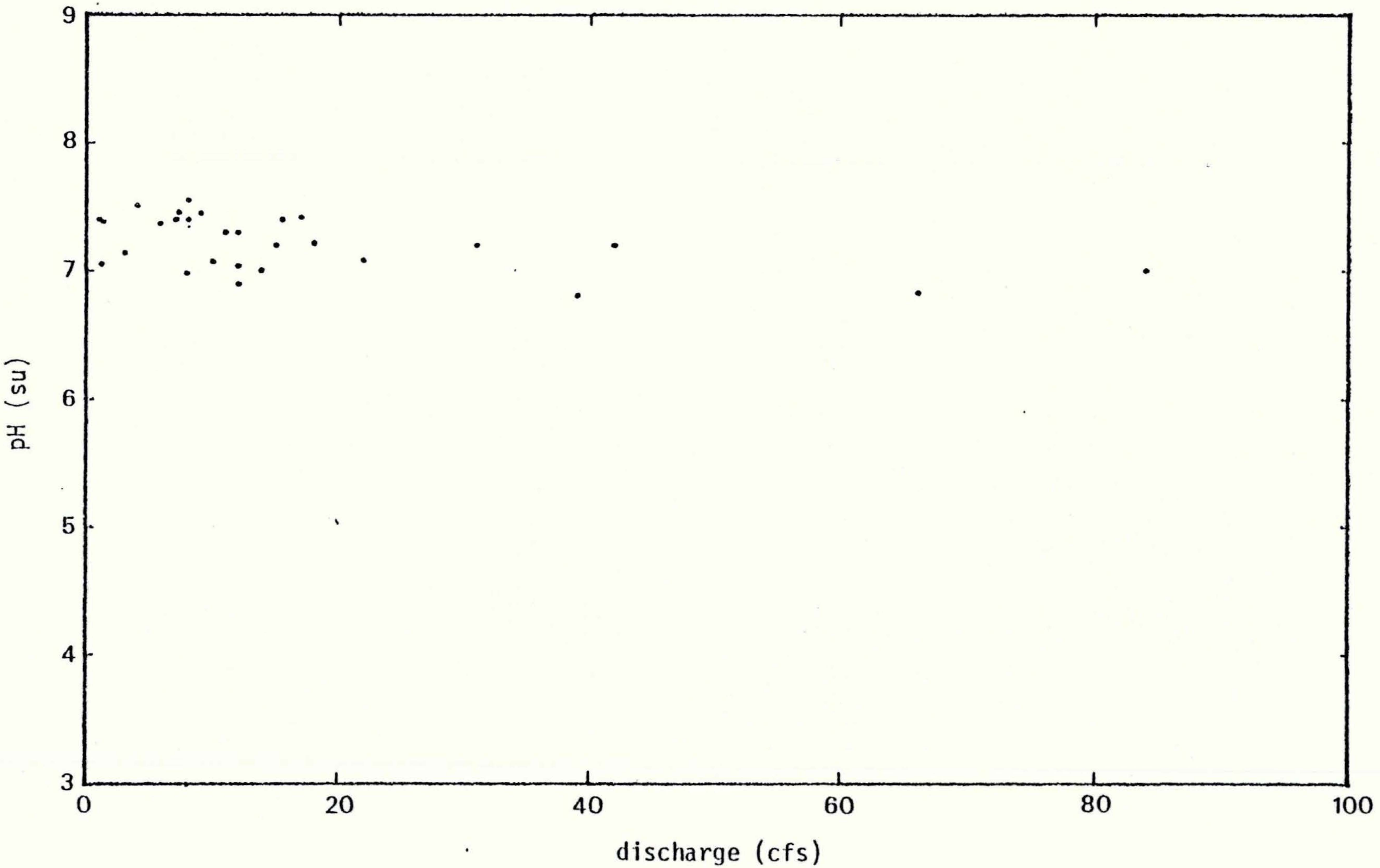

Figure 14. pH versus discharge, site 100.

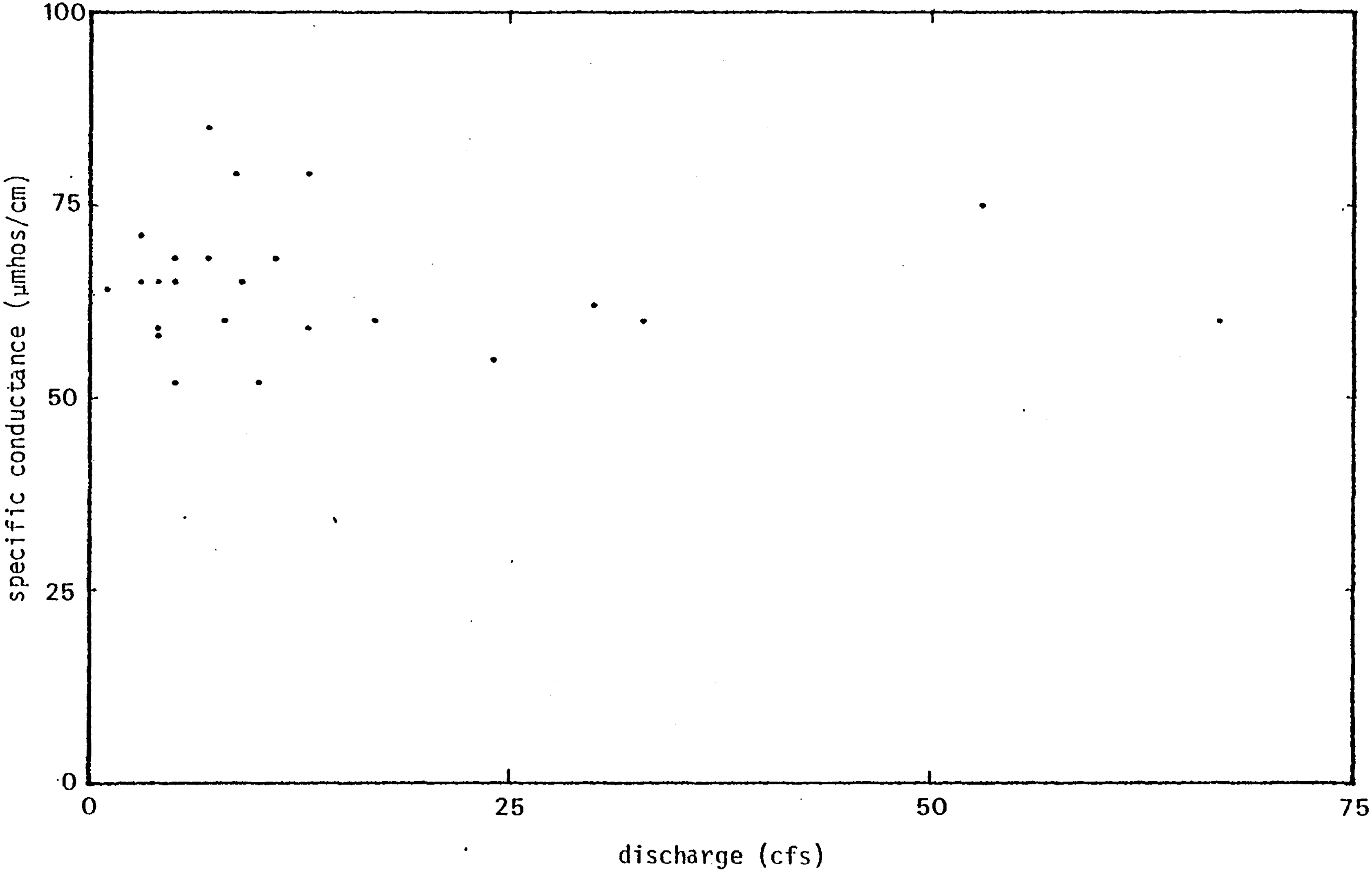

Figure 15. Specific conductance versus discharge, site 150.

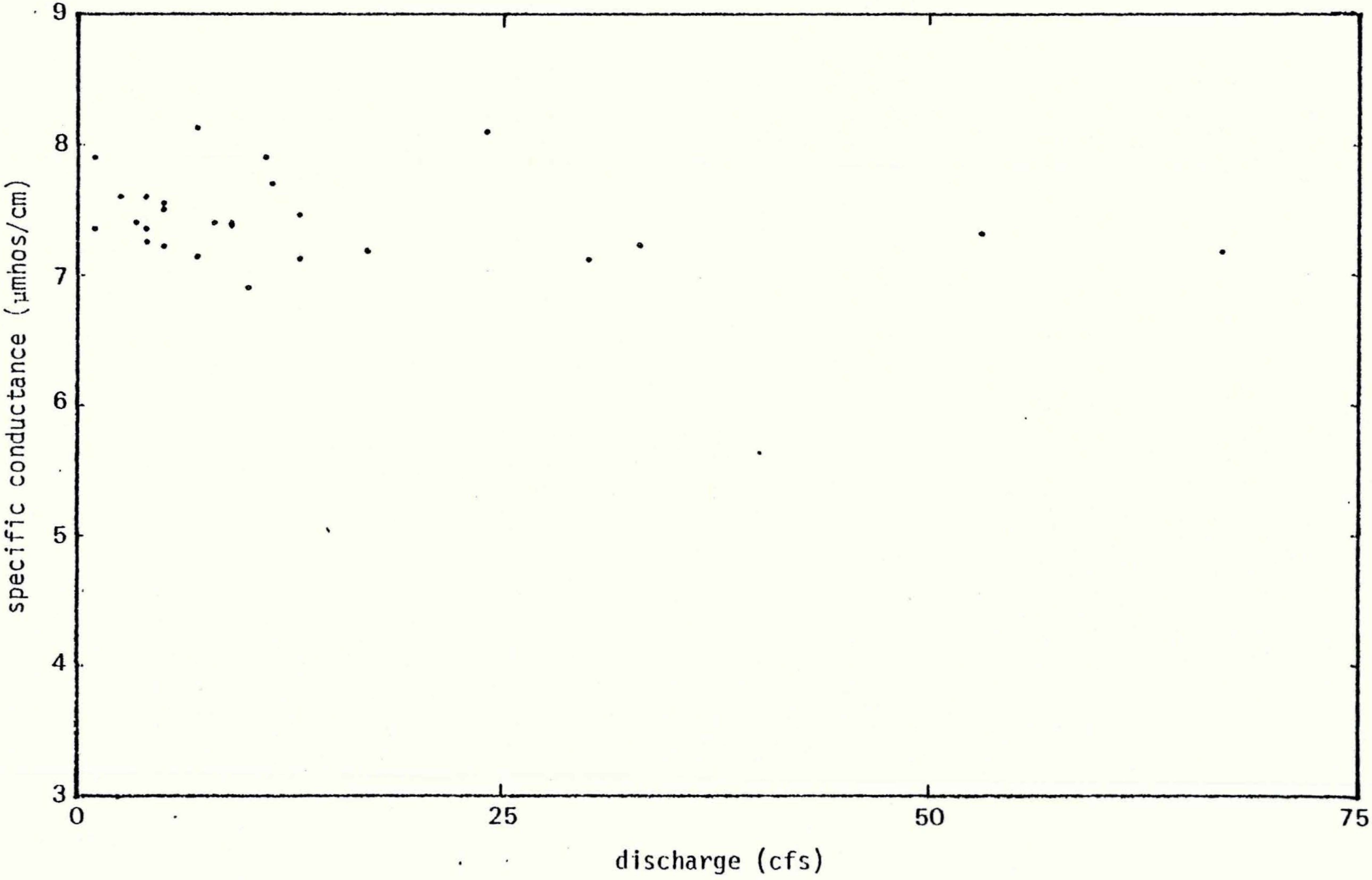

Figure 16. pH versus discharge, site 150.

there was no need to account for a dilution phenomenon and, therefore, no need for the mass-balance functions. However, the data did appear to lend itself to an area weighing approach similar to that proposed by Haupt and Snyder (1978). The proposed functions now took the forms:

$$\hat{SC} = \Sigma A_i f(SC_i) \qquad [5]$$

and

$$\hat{pH} = -\log \Sigma A_i f(H_i) \qquad [6]$$

where $\hat{SC}$ and $\hat{pH}$ are estimated mean specific conductance and mean pH, A_i is the percent of the total basin area occupied by the i^{th} complex, $f(SC_i)$ is a dissolved solids dissolution index function (µmhos/cm) for the i^{th} complex and $f(H_i)$ is an excess hydrogen ion dissolution index function (M/l) for the i^{th} complex.

Function Development and Application

Function Development

Haupt and Snyder, when applying a function of this type, estimated the dissolution index functions using an iterative trial and error procedure. The functions were found to vary with the percent of total basin area occupied by a complex in either exponential or linear form as shown in Figure 2 (p.8). In this study, the dissolution index functions were estimated using a least squares non-linear regression program from the Statistical Package for the Social Sciences (1975). Mean specific conductance and pH data, along with the percent of the soil and geologic complexes drained by each site on the Little Black

Fork basin, were regressed through exponential, linear and power equations to obtain a statistical best-fit estimate of the various dissolution index functions.

Regression equations. The exponential, linear and power function regression equations are listed in Table 13. Constraints were placed on the regression coefficients of each equation to prevent the dissolution index functions from being negative as well as decreasing as the percent of the areal exposure of a complex (A_i) increases.

Complex delineation. Soil boundaries were used to delineate or define complex types in most of the regression functions since they appeared to coincide with changes in stream chemistry more strongly than geologic boundaries. Therefore, the Pottsville complex was assumed to occupy all of the area above the Ernest-Dekalb and Penn-Meckesville soil boundary while the Mauch Chunk complex was assumed to occupy the area between this soil boundary and the Belmont-Meckesville boundary. The proportion of the various complexes exposed in the drainage of each site was determined using delineations of this type; however, only the areal extent of the Pottsville and Mauch Chunk complexes were substantially affected. The areal exposure of the other rock types correspond very well to the exposure of their associated soil series and, therefore, these complexes were not greatly affected.

Table 13. Regression equations used to estimate dissolution index functions.

Dissolution Index	Regression Equations[1]	
Function	Specific Conductance	pH
Exponential	$\overline{SC} = {}_{i}A_{i}(a_{i}e^{b_{i}A_{i}})$	$\overline{pH} = -\log\ {}_{i}A_{i}(a_{i}e^{b_{i}A_{i}})$
Linear	$\overline{SC} = {}_{i}A_{i}(a_{i} + b_{i}A_{i})$	$\overline{pH} = -\log\ {}_{i}A_{i}(a_{i} + b_{i}A_{i})$
Power	$\overline{SC} = {}_{i}A_{i}(a_{i}A_{i}{}^{b}i)$	$\overline{pH} = -\log\ {}_{i}A_{i}(a_{i}A_{i}^{b_{i}})$

---

[1] $\overline{SC}$ is the mean observed specific conductance, $\overline{pH}$ is the mean observed pH, A_i is the percent of total basin area occupied by the ith complex and a_i and b_i are regression coefficients associated with the ith complex.

Seven separate functions were developed for the estimation of both specific conductance and pH. One exponential function (A) was formulated with geologic boundaries to test the assumption that areal extent of the soil series corresponds to stream chemistry more strongly than areal extent of the geologic groups. Three functions (B, C and D), one of each function type (exponential, linear and power), were developed using soil boundaries to delineate between complex types. In addition, three functions (E, F and G) were developed, again one of each type, in which the Very Stony Land - Dekalb soil type was treated as a separate complex since this soil appeared to affect stream chemistry in a substantially different manner than the rest of the Pottsville complex.

Specific conductance functions. Results of the seven specific conductance functions are given in Table 14. The root mean square residual (RMSR) values are relative indicators of a goodness of fit and denote the square root of the mean of the residuals squared. RMSR values correspond roughly to the average residual, or error, between predicted and observed values.

The function with the largest residuals or errors was the one developed with geologic boundaries delineating between complex types (function A). The RMSR of this function (29.1) was substantially larger than for the other six functions.

Functions B, C and D, which were developed with soil boundary delineations, all yielded similar results. Of these three functions,

Table 14. Results of the specific conductance functions.

Site	Obser. S.C.	Exponential Geologic Boundaries (A)	Exponential Soil Boundaries (B)	Power Soil Boundaries (C)	Linear Soil Boundaries (D)	Exponential, Separate VSL-Dekalb Complex (E)	Power, Separate VSL-Dekalb Complex (F)	Linear, Separate VSL-Dekalb Complex (G)
RMSR		29.1	19.5	19.4	20.2	19.2	18.1	19.4
100	65	54	58	59	61	57	54	57
110	64	54	60	61	64	59	57	59
120	65	56	61	64	65	61	59	60
130	66	63	64	68	68	63	63	63
140	68	64	66	69	69	65	65	64
150	65	62	64	66	66	66	63	62
160	63	61	62	64	64	61	61	61
170	63	58	58	59	59	57	57	57
180	42	49	50	48	49	49	49	49
190	35	43	40	39	39	40	41	41
210	43	44	42	39	46	42	35	40
310	203	154	165	164	170	165	169	168
200	30	41	34	34	34	35	36	35
410	33	41	33	32	32	34	34	34
500	28	40	35	35	35	35	36	35
220	30	39	37	35	42	37	30	35
230	32	15	17	29	15	17	29	17
241	77	161	101	107	110	102	103	103
251	35	105	80	86	91	80	30	92
261	139	135	172	170	176	172	176	175
271	216	140	179	183	178	175	185	177
242	32	30	29	25	31	29	24	28
252	25	18	17	22	15	17	24	17
272	22	15	17	29	15	17	29	17
131	22	69	63	65	67	55	45	54
320	263	244	266	231	247	255	252	258
340	155	129	128	132	127	130	128	127
350	77	113	119	113	112	120	117	120
151	153	133	134	142	142	135	141	138
152	180	187	182	184	186	183	190	186
181	132	124	129	133	129	131	130	128
182	77	93	80	79	79	77	75	77
183	71	92	86	82	82	83	81	84
191	40	53	55	63	62	59	60	61
420	38	38	32	31	32	36	36	36
430	48	37	31	33	31	28	27	25
440	49	38	38	35	34	48	48	49
450	56	38	39	36	35	56	55	55
501	30	38	34	33	33	35	35	35
510	31	38	33	33	33	31	30	29
511	25	38	31	31	31	32	33	32
520	29	40	32	32	31	35	36	35
531	37	43	31	32	31	28	27	25
540	22	44	32	33	31	27	25	24

the power function (C) had the lowest RMSR (19.4) but was only slightly lower than the RMSR's of the exponential (19.5) and linear (20.2) functions.

Functions E, F and G, formulated with the Very Stony Land-Dekalb soil as a separate complex, had the smallest residuals of the seven functions tested. In particular, the residuals were smaller for sites 440 and 450, where the pyrite oxidation associated with the Very Stony Land-Dekalb soil is greatest.

Power function F, which utilized a separate complex for the Very Stony Land - Dekalb soil, was selected as the best function to predict specific conductance. An illustration of the dissolution index functions is shown in Figure 17. The dissolution index functions are plotted only for the range of data from which they were developed. From this graph, dissolution index values for each complex can be estimated and then substituted into equation [5] to predict mean specific conductance in μmhos/cm. As was expected, the dissolution index function for the easily weathered Greenbriar complex was the largest, and the dissolution index functions for the resistant Pottsville, Pocono and Hampshire groups were the smallest.

Function F was selected for several reasons. First, it yielded the smallest residuals of all the functions. A plot of the predicted versus observed specific conductance for this function is shown in Figure 18. Simulated mean specific conductance was within five μmhos/cm of the observed mean specific conductance for 24 sites and within 10 μmhos/cm for 32 sites. Generally, the largest errors of prediction occurred at sites draining a large proportion of the Greenbriar complex.

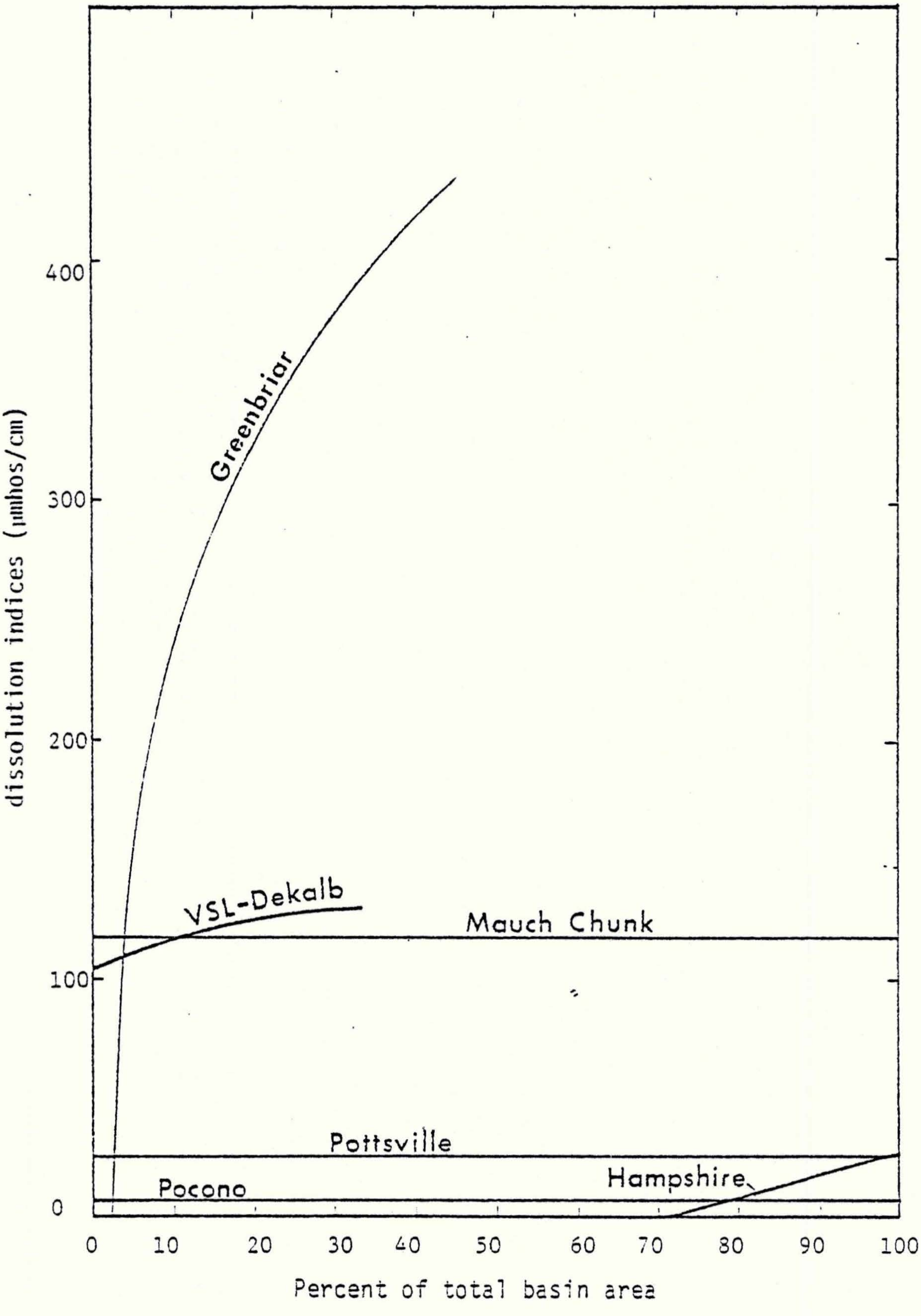

Figure 17. Specific conductance dissolution indices.

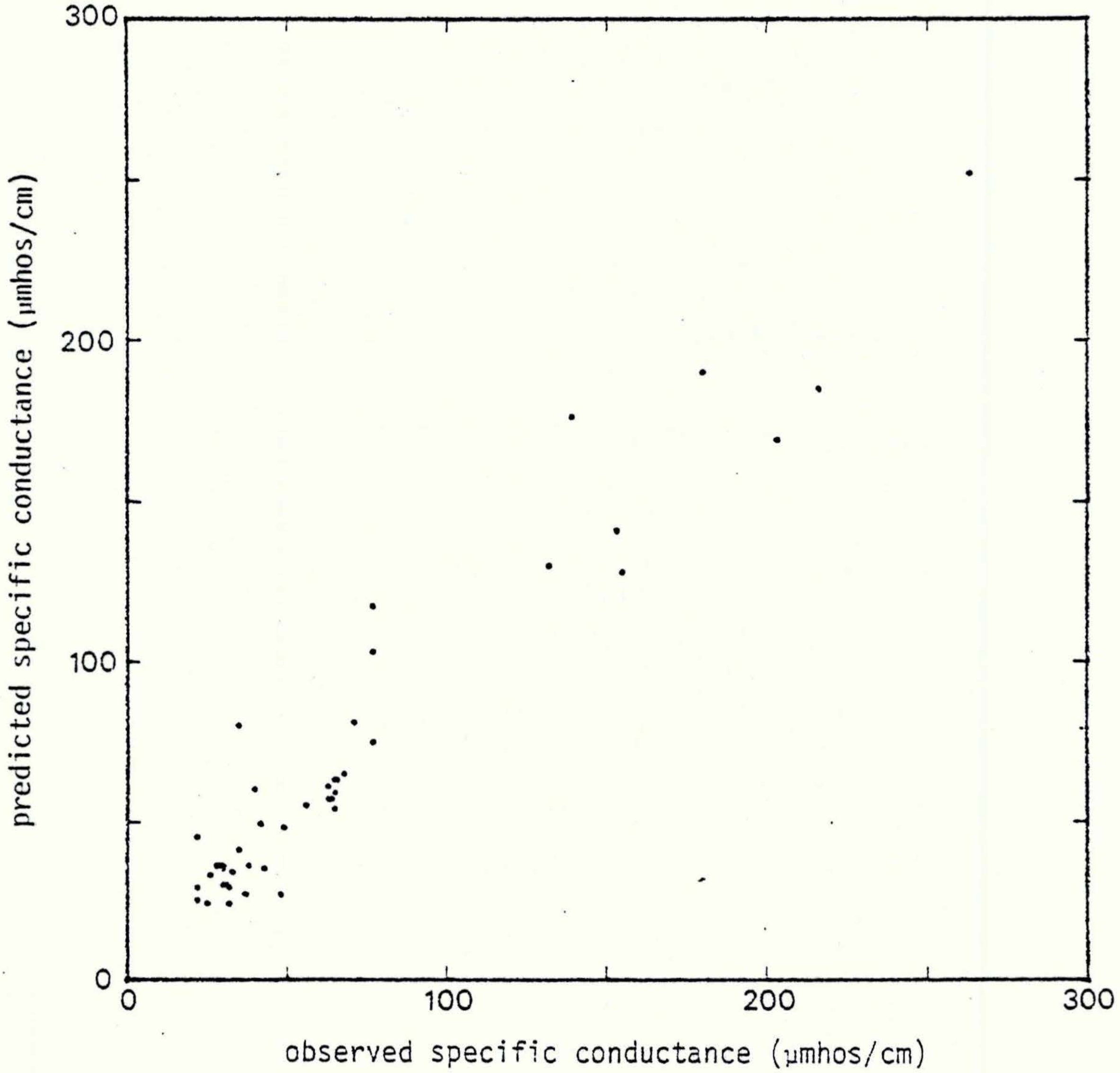

Figure 18. Observed versus predicted mean specific conductance.

Second, the power dissolution functions, as illustrated in Figure 17, appear to approximate the relationship between dissolution index and the percent of area occupied by a complex more accurately than the linear of exponential functions. It would be expected that as the percent of drainage area occupied by a complex increases, a threshold would be reached where the dissolution index would plateau, or increase at a slower rate. The linear, and in particular the exponential dissolution function, cannot account for this plateau and must increase at a constant or exponential rate as the percent of drainage area occupied by a complex increases. Power function indices, on the other hand, are able to level off and possibly approximate the actual phenomenon more accurately.

pH functions. Of the seven pH functions, power function F was again chosen as the best. The results of function F are summarized in Table 15 and a plot of the simulated versus observed mean pH is shown in Figure 19. The RMSR for this pH function was 0.4 indicating an approximate mean residual of 0.4 standard units. For 20 of the sampling sites, residuals were within 0.2 standard units. A residual greater than 0.5 standard units occurred at only four sites.

A plot of the excess hydrogen ion dissolution index functions, along with the regression coefficients for the selected pH function, is illustrated in Figure 20. A dissolution index for the Greenbriar complex is not included in this figure. The Greenbriar complex released such few excess hydrogen ions that the dissolution index for the complex

Table 15. Mean observed pH and predicted results of pH function F.

Site	Observed Mean pH (su)	Predicted Mean pH (su)
100	7.17	7.36
110	7.23	7.37
120	7.23	7.41
130	7.20	7.36
140	7.22	7.27
150	7.35	7.20
160	7.27	7.08
170	7.35	6.94
180	6.99	6.52
190	6.40	5.85
210	6.96	6.46
310	7.79	7.41
200	5.43	5.38
410	5.81	5.42
500	5.14	5.29
220	6.30	6.43
230	6.20	6.24
241	7.09	6.89
251	6.26	6.69
261	7.42	7.39
271	7.77	7.44
242	6.54	6.36
252	6.17	6.26
272	6.18	6.24
131	6.45	6.90
320	7.99	7.69
340	7.56	7.34
350	7.39	7.29
151	7.57	7.34
152	7.86	7.55
181	7.33	7.35
182	7.11	7.59
183	7.12	7.50
191	6.68	7.42
420	4.52	5.33
430	4.36	4.59
440	4.23	4.23
450	4.07	3.83
501	5.55	5.33
510	4.89	4.84
511	5.41	5.00
520	4.61	5.00
530	4.33	5.12
531	4.41	4.61
540	4.83	4.49

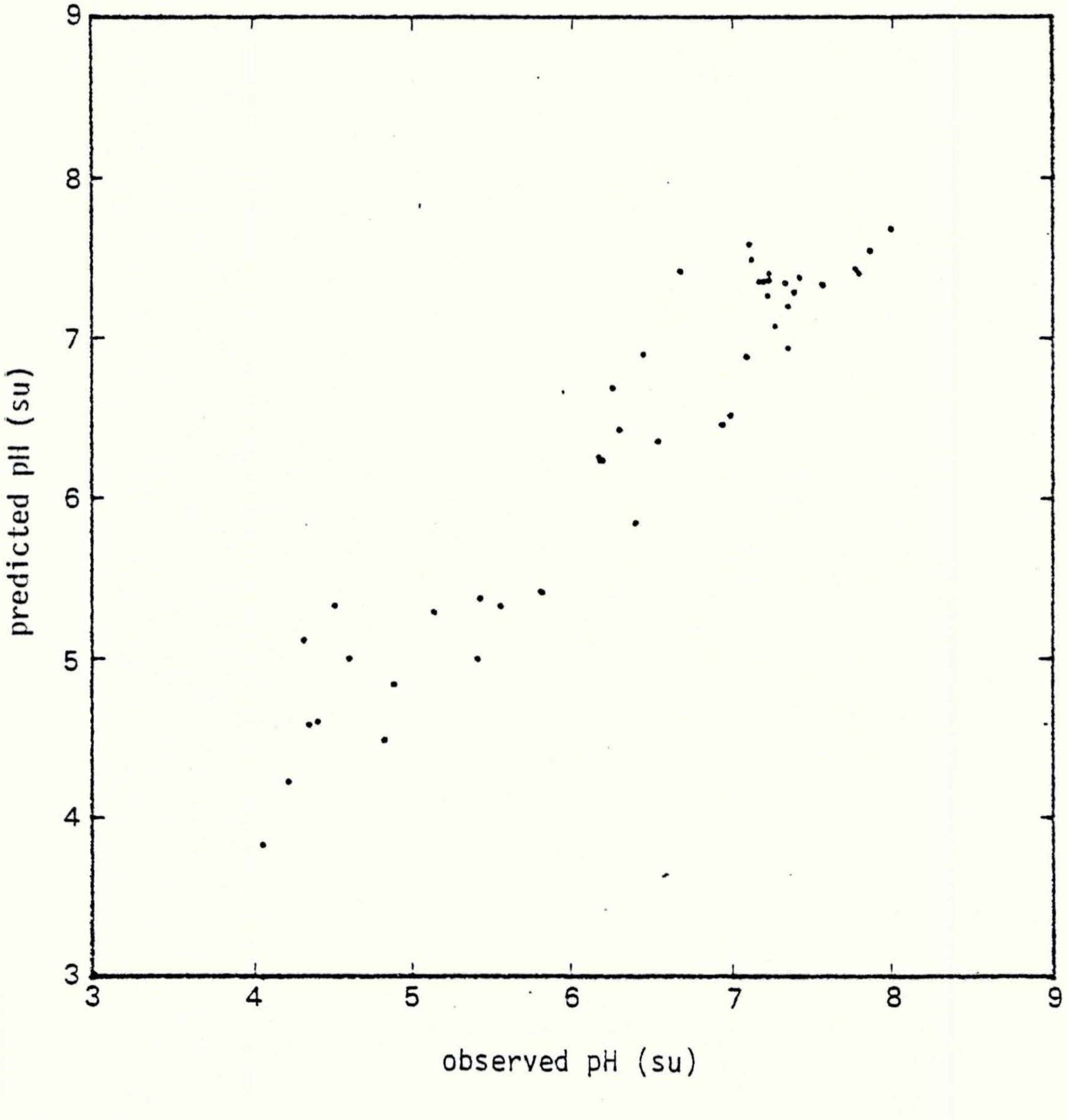

Figure 19. Observed versus predicted mean pH.

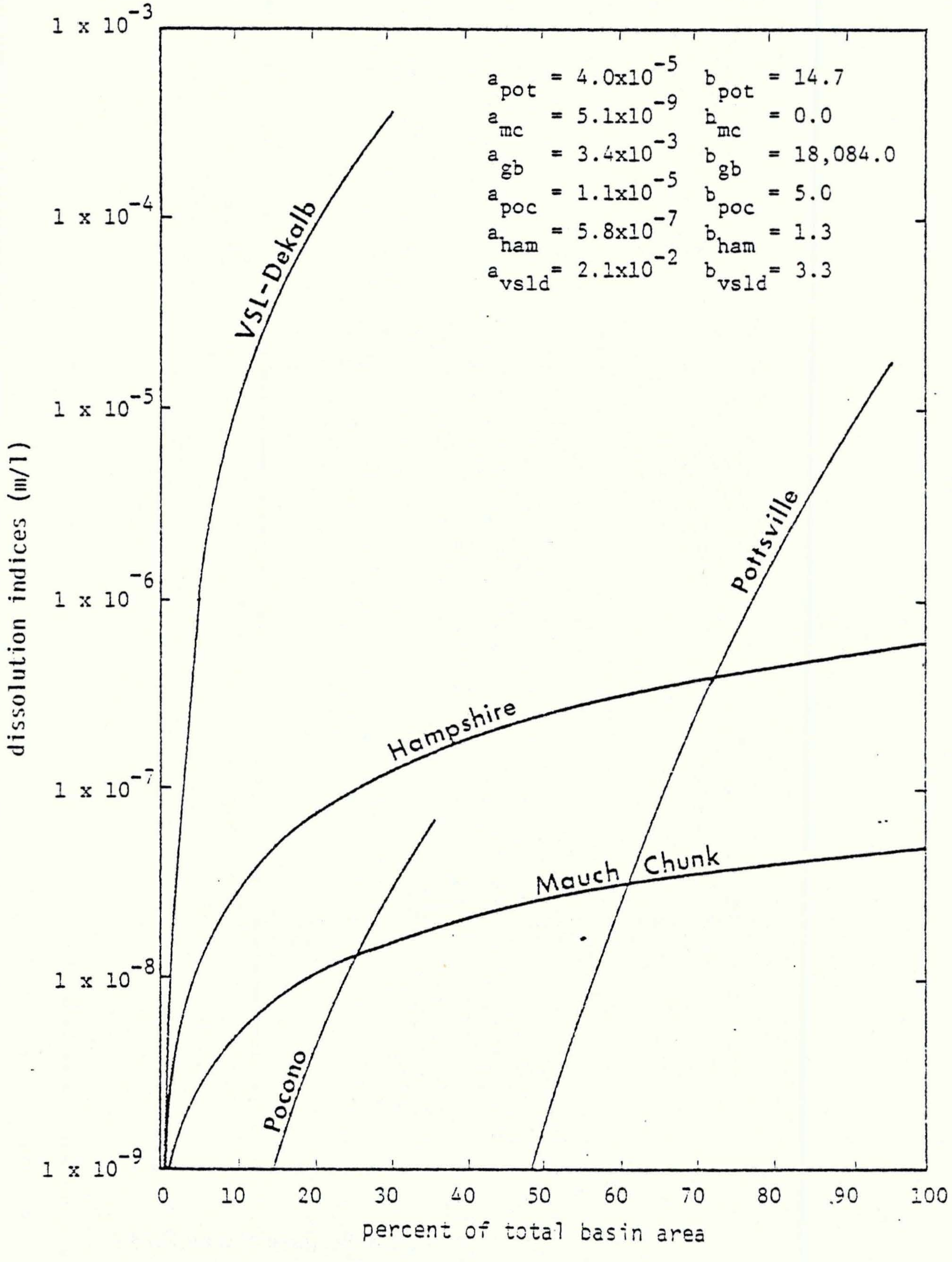

Figure 20. pH function dissolution indices and regression coefficients.

did not fall into the range of the other index functions plotted. In order to estimate the dissolution index for this complex the appropriate regression coefficients along with the percent of area occupied by the complex can be substituted into the power dissolution index function. Dissolution index values for each complex may be substituted into equation [6] for the estimation of mean pH.

Application of the Selected Specific Conductance and pH Functions

The selected mean specific conductance and pH functions were applied to four watersheds adjacent to the study area, for which limited geologic and water quality data were available. The data and function results for these watersheds are summarized in Table 16. Since no soil information was available, two assumptions were involved in the application of the water quality functions to these areas. First, soil boundaries were assumed to coincide with geologic boundaries. Second, the Pottsville complex of these watersheds was assumed to be uniform in nature with with no increased amount of pyrite oxidation as related to the Very Stony Land-Dekalb soil complex of the Little Black Fork basin.

The specific conductance function predicted mean observed conductance with fair accuracy for two of the watersheds. Simulated mean specific conductances for Whit Meadow Run and Taylor Run were within six and eight μmhos/cm, respectively, of the observed specific conductance. These two watersheds are similar to or have a smaller drainage area than the Little Black Fork basin. Mean specific conductance predictions for the other two basins, Laurel

Table 16. Specific conductance and pH function results for watersheds adjacent to the study area.

Watershed	Drainage Area (ha)	Percent of Geologic Groups Exposed	Mean Specific Conductance (μmhos/cm)		Mean pH (su)	
			Observed	Simulated	Observed	Simulated
Whit Meadow Run	780	Pottsville - 94% Mauch Chunk - 6%	23	29	4.7	4.9
Taylor Run	1,310	Pottsville - 54% Mauch Chunk - 45% Greenbriar - 1%	74	66	6.8	7.9
Laurel Fork	11,400	Mauch Chunk - 5% Greenbrian - 2% Pocono - 4% Hampshire - 89%	73	20	7.5	6.4
Shavers Fork at Bemus	29,800	Pottsville - 65% Mauch Chunk - 35%	29	56	6.2	7.3

Fork and Shavers Fork at Bemus, were poor. The prediction error may be due to the underlying assumptions involved in the application of the functions or due to the large size of the Laurel Fork and Shavers Fork watersheds. The specific conductance function was developed on drainage areas of only 1230 ha or smaller.

Simulated results from the pH function exhibited considerable error. Only for one watershed, Whit Meadow Run, was the predicted mean pH within one standard unit of the mean observed pH. Results for the other three watersheds all varied substantially from the mean observed pH, possibly due to assumptions involved in the function application or the simplified nature of predictive function.

It should be noted that the pH function (equation [6]) is a simple addition function which sums excess hydrogen ions released by each complex. The function does not directly take into account the buffering effect of alkalinity upon pH or the complex equilibrium conditions which govern the transport and release of hydrogen ions in a natural system. As a result, this simplisitic pH function was felt to be extremely site specific and applicable only to the watershed for which it is quantified. In order to simulate pH in a more thorough manner, it is recommended that a mass-balance approach be utilized, where hydrologic and water quality data for the complete range of hydrologic conditions are available, in conjunction with the use of soil and rock water extracts to determine the buffering characteristics of each complex type.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Several conclusions can be drawn from the results of this study:

1. Cluster analysis was a very powerful tool in the interpretation of the water quality data. While the analysis was subject to several limiting conditions, it provided an objective means to group sites with similar water quality characteristics. From these clusters the relationships between stream chemistry and soil and geologic complexes could be more easily defined.

2. No relationship between specific conductance or pH and discharge was apparent at sites for which streamflow was simulated.

3. Waters associated with the sandstone Pottsville group and its derived soils are acid in nature with low dissolved solids concentrations. Localized exposure of pyritic material within the complex further increases the acidity of stream waters at several sites.

4. Waters draining substantial proportions of the carbonate Greenbriar complex are typified by a basic pH and substantially increased specific conductance, alkalinity, calcium and magnesium concentrations.

5. Waters associated with the Mauch Chunk complex also exhibit increased carbonate influence but not to the degree of waters associated with the Greenbriar complex.

6. The chemistry of stream waters draining the Hampshire complex is typified by low dissolved solids concentrations, a neutral to slightly acidic pH and increased potassium concentrations.

7. Due to the heterogenetic properties of the soil series and rock groups present, and the complexity of the hydrologic and chemical dissolution processes, an effective prediction procedure for stream chemistry cannot be developed with the data available to this study.

Recommendations for Further Study

In order to more fully evaluate and quantify the relationship between stream chemistry and the soil and rock complexes exposed on the Monongahela National Forest, several areas of additional study are recommended.

1. More water quality samples should be collected at sites draining a single complex type, particularly the Pocono, Greenbriar and Mauch Chunk complexes. Discharge measurements should be taken to correspond with each water quality sample. This would provide valuable information concerning not only the baseline water quality but also the natural variation in stream chemistry for a single complex.

2. The frequency of additional water quality sampling should be geared not to regular weekly or monthly intervals, but to hydrologic response. Most of the samples for this study were collected

during baseflow and therefore provide little information concerning stream chemistry during different flow regimes.

3. Soil-water and rock-water extracts should be analyzed to determine the equilibrium conditions and buffering capacities common to each complex.

4. Water pathways and discharge rates should be determined for each soil and rock complex. Before an accurate predictive function for stream chemistry can be developed, an estimate of which complexes the water has been in contact with and the proportion of the total stream discharge derived from each complex type is needed.

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APPENDIX

Mean, Standard Deviation and Range of the Water Quality Parameters of Each Site

	Specific Conduct. (μmhos/cm)	Hydrogen Ion Activity (m/l)	Acidity (mg/l as $CaCO_3$)	Alkalinity (mg/l as $CaCO_3$)	Iron (mg/l)	Sulfate (mg/l)	Nitrate (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Potassium (mg/l)
Site 100											
Mean	64.86	0.67×10^{-7}	2.31	16.98	0.06	8.46	1.00	8.59	0.91	0.91	0.72
Std.Dev.	6.98	0.35×10^{-7}	0.72	3.48	0.03	1.83	0.38	2.21	0.24	0.28	0.36
Range	52-83	0.3×10^{-7}-0.2×10^{-6}	1.5-4.2	12-28	0.02-0.10	6.0-13.0	0.44-2.00	4.8-17.9	0.40-1.46	0.46-1.56	0.27-1.69
Site 110											
Mean	64.86	0.58×10^{-7}	2.07	17.46	0.06	8.57	0.86	8.70	0.92	0.88	0.56
Std.Dec.	7.47	0.30×10^{-7}	0.57	3.85	0.02	2.16	0.32	2.30	0.21	0.27	0.15
Range	50-89	0.2×10^{-7}-0.3×10^{-6}	1.0-4.0	12-31	0.02-0.10	5.0-13.5	0.40-1.90	5.1-17.9	0.55-1.46	0.42-1.60	0.27-1.14
Site 120											
Mean	64.89	0.58×10^{-7}	2.13	17.88	0.06	8.31	0.88	8.73	0.91	0.87	0.63
Std.Dev.	8.13	0.31×10^{-7}	0.65	4.05	0.03	1.77	0.35	2.41	0.30	0.25	0.51
Range	50-89	0.2×10^{-7}-0.1×10^{-6}	1.0-4.0	12-28	0.03-0.12	5.0-13.0	0.20-1.70	4.8-17.9	0.55-1.96	0.49-1.73	0.18-3.06
Site 210											
Mean	43.00	0.12×10^{-6}	2.16	10.35	0.06	7.78	0.65	4.19	0.82	0.88	0.97
Std.Dev.	5.08	0.44×10^{-7}	0.69	2.78	0.03	1.98	0.39	0.81	0.22	0.22	0.23
Range	37-54	0.6×10^{-7}-0.2×10^{-6}	1.0-4.5	6-18	0.02-0.13	5.0-13.0	0.02-1.71	2.9-5.9	0.30-1.25	0.50-1.77	0.46-1.65
Site 220											
Mean	30.05	0.50×10^{-6}	2.71	4.17	0.06	7.48	0.60	1.87	0.71	0.89	0.87
Std.Dev.	6.75	0.31×10^{-6}	0.94	0.98	0.03	2.08	0.50	0.48	0.18	0.21	0.22
Range	26-39	0.8×10^{7}-0.1×10^{-5}	1.0-4.5	3-7	0.00-0.13	5.0-12.5	0.00-2.34	0.6-2.9	0.40-1.25	0.60-1.32	0.36-1.43
Site 230											
Mean	32.82	0.62×10^{-6}	2.41	5.14	0.06	7.95	0.71	2.29	0.81	0.89	0.82
Std.Dev.	6.75	0.42×10^{-6}	0.38	4.70	0.03	2.46	0.31	1.48	0.18	0.30	0.18
Range	24-46	0.1×10^{-6}-0.2×10^{-5}	2.0-3.0	2-15	0.02-0.12	5.0-13.0	0.05-1.10	0.2-6.0	0.60-1.18	0.54-1.36	0.36-1.06

	Specific Conduct. (μmhos/cm)	Hydrogen Ion Activity (M/L)	Acidity (mg/l as $CaCO_3$)	Alkalinity (mg/l as $CaCO_3$)	Iron (mg/l)	Sulfate (mg/l)	Nitrate (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Potassium (mg/l)
Site 241											
Mean	78.17	0.82×10^{-7}	2.63	25.90	0.07	8.46	0.91	9.91	1.08	1.10	0.86
Std. Dev.	16.17	0.89×10^{-7}	0.63	5.28	0.04	1.79	0.45	3.28	0.30	0.23	0.23
Range	22-101	$0.3 \times 10^{-7}-0.5 \times 10^{-6}$	1.5-4.0	18-35	0.02-0.22	6.0-13.5	0.45-2.13	0.9-13.9	0.58-1.73	0.75-1.67	0.36-1.43
Site 251											
Mean	35.70	0.55×10^{-6}	2.78	4.68	0.07	8.10	0.84	1.93	0.88	1.05	0.95
Std.Dev.	3.67	0.29×10^{-6}	1.33	3.33	0.03	1.66	0.47	0.68	0.20	0.22	0.45
Range	30-47	$0.2 \times 10^{-6}-0.1 \times 10^{-5}$	1.5-7.5	3-18	0.0-0.14	6.0-12.5	0.32-2.34	0.2-2.7	0.40-1.31	0.68-1.71	0.36-2.63
Site 261											
Mean	139.65	0.38×10^{-7}	2.85	52.72	0.07	10.12	1.28	19.06	1.54	1.21	0.89
Std.Dev.	23.8	0.20×10^{-7}	0.87	11.49	0.03	1.82	0.69	5.70	0.44	0.31	0.35
Range	79-178	$0.2 \times 10^{-7}-0.1 \times 10^{-6}$	1.5-5.5	36-74	0.02-0.16	7.0-14.5	0.5203.40	1.8-27.0	0.75-2.59	0.80-2.06	0.27-2.12
Site 271											
Mean	216.57	0.17×10^{-7}	3.02	90.11	0.08	10.45	1.69	26.57	1.97	1.15	0.82
Std.Dev.	30.89	0.80×10^{-8}	1.22	15.26	0.05	1.84	0.72	9.21	0.47	0.40	0.40
Range	118-260	$0.8 \times 10^{-8}-0.4 \times 10^{-7}$	1.0-5.5	60-116	0.0.-0.24	6.0-15.0	0.56-3.40	0.6-39.6	1.22-3.23	0.54-2.10	0.27-1.88
Site 242											
Mean	31.38	0.28×10^{-6}	2.44	5.46	0.08	6.86	0.61	2.13	0.70	0.78	0.93
Std.Dev.	3.29	0.19×10^{-6}	0.90	1.40	0.04	2.06	0.46	0.66	0.17	0.17	0.25
Range	24-40	$0.2 \times 10^{-7}-0.1 \times 10^{-5}$	1.0-5.5	4-9	0.2-0.16	3.0-12.5	0.00-2.00	0.2-3.1	0.40-1.17	0.54-1.20	0.46-1.71
Site 252											
Mean	25.27	0.68×10^{-6}	3.23	3.80	0.10	6.78	0.48	1.45	0.65	0.92	0.85
Std.Dev.	3.40	0.43×10^{-6}	1.56	0.90	0.11	2.81	0.36	0.47	0.20	0.38	0.29
Range	16-32	$0.6 \times 10^{-7}-0.2\times10^{-5}$	1.0-8.5	3-6	0.3-0.55	0.0-12.0	0.00-1.20	0.1-2.4	0.30-1.05	0.54-2.23	0.36-1.80

	Specific Conduct. (μmhos/cm)	Hydrogen Ion Activity (m/ℓ)	Acidity (mg/l as $CaCO_3$)	Alkalinity (mg/l as $CaCO_3$)	Iron (mg/l)	Sulfate (mg/l)	Nitrate (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Potassium (mg/l)
Site 262											
Mean	48.73	0.15×10^{-6}	2.80	12.14	0.08	7.99	0.72	4.81	0.94	0.85	0.94
Std. Dev.	5.07	0.71×10^{-7}	0.90	2.61	0.04	1.99	0.39	1.56	0.26	0.23	0.27
Range	34-60	0.6×10^{-7}-0.3×10^{-6}	1.0-4.5	9-17	0.01-0.20	5.0-12.5	0.05-1.68	0.5-7.0	0.40-1.41	0.62-1.77	0.36-1.71
Site 272											
Mean	22.76	0.66×10^{-6}	2.93	3.93	0.12	6.85	0.82	2.11	0.57	0.87	0.80
Std.Dev.	2.39	0.42×10^{-6}	0.97	1.78	0.05	2.37	0.88	3.54	0.39	0.48	0.28
Range	16-26	0.6×10^{-7}-0.1×10^{-5}	1.0-5.5	2-9	0.03-0.22	3.0-12.0	0.08-3.80	0.1-17.1	0.24-2.08	0.55-2.40	0.36-1.71
Site 130											
Mean	67.29	0.63×10^{-7}	2.10	17.84	0.06	8.02	0.93	8.87	0.91	0.93	0.56
Std.Dev.	8.70	0.30×10^{-7}	0.61	4.86	0.03	2.05	0.35	1.59	0.19	0.33	0.24
Range	52-92	0.2×10^{-7}-0.1×10^{-6}	1.0-3.5	9-34	0.00-0.13	3.0-11.0	0.40-1.69	5.1-13.9	0.55-1.25	0.60-2.11	0.27-1.43
Site 131											
Mean	32.15	0.36×10^{-6}	2.51	3.85	0.08	8.71	0.53	1.75	0.81	1.27	0.78
Std.Dev.	3.05	0.24×10^{-6}	0.60	0.77	0.05	2.06	0.42	0.44	0.32	0.94	0.16
Range	26-38	0.2×10^{-7}-0.8×10^{-6}	1.5-3.5	3-6	0.02-0.20	6.0-12.5	0.00-1.70	1.1-2.9	0.40-1.67	0.77-4.05	0.36-0.93
Site 140											
Mean	67.50	0.61×10^{-7}	2.12	18.71	0.07	8.24	0.97	8.91	0.90	0.89	0.51
Std.Dev.	10.76	0.30×10^{-7}	0.53	5.70	0.01	1.88	0.36	1.89	0.23	0.26	0.23
Range	49-101	0.2×10^{-7}-0.1×10^{-6}	1.0-3.0	9-38	0.02-0.18	5.0-11.6	0.46-1.81	5.3-15.7	0.55-1.25	0.43-1.77	0.18-1.29
Site 272											
Mean	22.76	0.66×10^{-6}	2.93	3.93	0.12	6.85	0.82	2.11	0.57	0.87	0.80
Std.Dev.	2.39	0.42×10^{-6}	0.97	1.78	0.05	2.37	0.88	3.54	0.39	0.48	0.28
Range	16-26	0.6×10^{-7}-0.1×10^{-5}	1.0-5.55	2-9	0.03-0.22	3.0-12.0	0.08-3.80	0.1-17.1	0.24-2.08	0.55-2.40	0.36-1.71

	Specific Conduct. (μmhos/cm)	Hydrogen Ion Activity (moles/l)	Acidity (mg/l as Ca CO$_3$)	Alkalinity (mg/l as CaCO$_3$)	Iron (mg/l)	Sulfate (mg/l)	Nitrate (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Potassium (mg/l)
Site 130											
Mean	67.29	0.63×10^{-7}	2.10	17.84	0.06	8.02	0.93	8.87	0.91	0.93	0.56
Std.Dev.	8.70	0.30×10^{-7}	0.61	4.86	0.03	2.05	0.35	1.59	0.19	0.33	0.24
Range	52-92	0.2×10^{-7}-0.1×10^{-6}	1.0-3.5	9-34	0.0-0.13	3.0-11.0	0.40-1.69	5.1-13.9	0.55-1.25	0.60-2.11	0.27-1.43
Site 131											
Mean	32.15	0.36×10^{-6}	2.51	3.85	0.08	8.71	0.53	1.75	0.81	1.27	0.78
Std.Dev.	3.05	0.24×10^{-6}	0.60	0.77	0.05	2.06	0.42	0.44	0.32	0.94	0.16
Range	26-38	0.2×10^{-7}-0.8×10^{-6}	1.5-3.5	3-6	0.2-0.20	6.0-12.5	0.00-1.70	1.1-2.9	0.40-1.67	0.77-4.05	0.36-0.93
Site 140											
Mean	67.50	0.61×10^{-7}	2.12	18.71	0.07	8.24	0.97	8.91	0.90	0.89	0.51
Std.Dev.	10.76	0.30×10^{-7}	0.53	5.70	0.03	1.88	0.36	1.89	0.23	0.26	0.23
Range	49-101	0.2×10^{-7}-0.1×10^{-6}	1.0-3.0	9-38	0.02-0.18	5.0-11.6	0.46-1.81	5.3-15.7	0.55-1.25	0.43-1.77	0.18-1.29
Site 310											
Mean	206.70	0.16×10^{-7}	2.41	87.20	0.08	11.43	1.12	28.10	1.94	1.01	0.77
Std.Dev.	29.82	0.13×10^{-7}	1.05	14.28	0.05	2.02	0.38	4.60	0.59	0.35	0.25
Range	165-310	0.6×10^{-8}-0.7×10^{-7}	1.0-6.0	65-123	0.02-0.31	7.0-17.0	0.35-1.85	18.8-36.8	0.47-3.81	0.49-2.17	0.18-1.43
Site 320											
Mean	263.64	0.10×10^{-7}	2.00	111.70	0.10	11.53	1.23	32.77	2.14	0.82	0.61
Std.Dev.	13.03	0.57×10^{-8}	1.29	25.99	0.06	2.10	0.45	7.09	0.62	0.19	0.26
Range	200-380	0.4×10^{-8}-0.3×10^{-7}	0.0-4.5	14-140	0.03-0.33	8.0-18.5	0.62-2.05	20.8-46.7	1.45-3.81	0.43-1.18	0.18-1.33
Site 330											
Mean	303.04	0.84×10^{-8}	1.81	135.69	0.07	11.98	1.41	31.99	2.30	0.82	0.51
Std.Dev.	38.72	0.47×10^{-8}	1.39	17.59	0.01	2.83	0.56	10.24	0.93	0.19	0.22
Range	200-415	0.3×10^{-8}-0.2×10^{-7}	0.0-5.0	78-157	0.01-0.10	3.0-19.5	0.57-2.81	1.0-50.1	0.35-4.30	0.42-1.15	0.18-1.26

	Specific Conduct. (μmhos/cm)	Hydrogen Ion Activity (moles/l)	Acidity (mg/l as Ca CO_3)	Alkalinity (mg/l as $CaCO_3$)	Iron (mg/l)	Sulfate (mg/l)	Nitrate (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Potassium (mg/l)
Site 140											
Mean	155.00	0.28×10^{-7}	3.77	61.63	0.08	10.31	1.09	18.09	1.32	0.93	0.52
Std.Dev.	87.91	0.14×10^{-7}	2.64	46.66	0.03	3.45	0.46	8.96	0.60	0.24	0.30
Range	82-315	0.5×10^{-8}-0.5×10^{-7}	1.5-9.5	21-147	0.02-0.13	5.0-19.0	0.23-1.90	8.0-40.4	0.55-2.47	0.60-1.54	0.18-1.43
Site 350											
Mean	77.05	0.40×10^{-7}	2.31	22.17	0.09	8.90	0.79	9.47	1.04	1.03	0.52
Std.Dev.	13.59	0.23×10^{-7}	0.54	4.69	0.04	2.03	0.42	2.09	0.30	0.18	0.18
Range	58-100	0.8×10^{-8}-0.1×10^{-6}	1.5-3.5	14-31	0.03-0.20	6.0-13.0	0.23-1.90	5.6-13.6	0.55-1.85	0.70-1.54	0.18-1.05
Site 150											
Mean	66.80	0.44×10^{-7}	2.16	18.33	0.07	8.66	1.01	8.47	0.88	0.87	0.53
Std.Dev.	10.06	0.25×10^{-7}	0.56	5.57	0.03	1.99	0.35	2.15	0.20	0.24	0.20
Range	52-100	0.7×10^{-8}-0.1×10^{-6}	1.0-3.5	11-39	0.00-0.12	4.0-13.0	0.45-1.78	4.3-15.7	0.60-1.27	0.42-1.37	0.18-1.18
Site 151											
Mean	152.60	0.27×10^{-7}	2.31	55.90	0.07	11.64	1.16	21.06	1.81	1.30	0.99
Std.Dev.	39.64	0.22×10^{-7}	0.79	10.64.	0.03	1.54	0.41	3.57	0.33	0.30	0.22
Range	118-283	0.1×10^{-7}-0.1×10^{-6}	1.2-4.5	39-74	0.03-0.13	8.1-14.5	0.45-2.00	16.0-27.6	1.26-2.65	0.77-1.93	0.46-1.52
Site 152											
Mean	180.29	0.14×10^{-7}	1.94	72.79	0.07	11.43	1.15	24.58	1.76	0.88	0.66
Std.Dev.	6.24	0.43×10^{-8}	0.72	11.59	0.03	2.57	0.57	2.72	0.90	0.18	0.12
Range	170-190	0.6×10^{-8}-0.2×10^{-7}	1.0-3.0	63-97	0.02-0.12	7.0-14.0	0.58-2.10	21.2-28.3	0.97-3.56	0.65-1.10	0.53-0.90
Site 160											
Mean	63.77	0.54×10^{-7}	2.08	17.68	0.07	8.21	1.02	8.26	0.87	0.82	0.48
Std.Dev.	10.66	0.36×10^{-7}	0.47	5.06	0.01	2.01	0.35	1.92	0.18	0.23	0.13
Range	48-100	0.1×10^{-7}-$0,2 \times 10^{-6}$	1.2-3.5	11-38	0.03-0.12	5.0-12.5	0.45-1.69	5.3-15.7	0.57-1.18	0.46-1.42	0.27-0.80

	Specific Conduct. (μmhos/cm)	Hydrogen Ion Activity (moles/l)	Acidity (mg/l as Ca CO$_3$)	Alkalinity (mg/l as CaCO$_3$)	Iron (mg/l)	Sulfate (mg/l)	Nitrate (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Potassium (mg/l)
Site 161											
Mean	312.00	0.11×10^{-7}	2.18	141.14	0.07	12.56	1.49	33.76	2.39	1.02	0.70
Std.Dev.	48.07	0.49×10^{-8}	1.27	23.99	0.03	1.44	0.49	7.54	0.83	0.26	0.18
Range	240-480	$0.4 \times 10^{-8}-0.2 \times 10^{-7}$	0.0-4.5	101-227	0.2-0.13	9.5-14.5	0.75-2.90	20.6-50.7	1.45-4.29	0.46-1.57	0.27-1.14
Site 170											
Mean	63.18	0.45×10^{-7}	2.20	15.84	0.06	7.87	1.05	7.80	0.85	0.82	0.52
Std.Dev.	10.56	0.23×10^{-7}	0.61	5.13	0.01	1.93	0.49	1.93	0.25	0.22	0.20
Range	47-95	$0.1 \times 10^{-7}-0.1 \times 10^{-6}$	1.0-3.5	9-35	0.02-0.12	3.0-11.0	0.41-2.80	4.4-14.5	0.45-1.42	0.46-1.43	0.18-1.29
Site 180											
Mean	42.07	0.10×10^{-6}	2.12	6.99	0.08	8.17	1.00	4.55	0.67	0.78	0.43
Std.Dev.	4.67	0.76×10^{-7}	0.75	1.78	0.03	2.30	0.50	0.95	0.16	0.30	0.12
Range	36-57	$0.1 \times 10^{-7}-0.3 \times 10^{-6}$	1.0-4.5	5-11	0.02-12	3.0-14.0	0.33-2.30	2.7-7.2	0.43-1.04	0.46-2.05	0.18-0.76
Site 181											
Mean	132.04	0.47×10^{-7}	2.03	43.10	0.06	9.96	1.46	18.45	1.44	1.17	0.67
Std.Dev.	42.04	$0.41 - 10^{-7}$	0.60	19.50	0.03	2.38	0.75	6.15	0.51	0.36	0.35
Range	91-255	$0.1 \times 10^{-7}-0.1 \times 10^{-6}$	1.5-3.5	17-79	0.02-0.12	5.0-13.5	0.44-3.90	9.5-28.9	0.42-2.65	0.46-2.15	0.18-1.98
Site 182											
Mean	77.00	0.77×10^{-7}	2.06	17.77	0.07	11.68	1.20	9.08	1.19	1.21	0.55
Std.Dev.	22.06	0.78×10^{-7}	0.74	11.17	0.04	1.90	0.37	4.08	0.28	0.31	0.21
Range	58-148	$0.2 \times 10^{-7}-0.3 \times 10^{-6}$	1.4-4.0	10-55	0.02-0.16	8.0-14.5	0.68-2.00	6.0-22.5	0.81-2.00	0.31-1.60	0.27-1.21
Site 183											
Mean	71.85	0.76×10^{-7}	2.06	15.90	0.08	11.68	1.20	7.48	1.24	1.29	0.57
Std.Dev.	11.23	0.63×10^{-7}	0.51	4.39	0.04	2.56	0.60	2.19	0.32	0.37	0.21
Range	56-110	$0.3 \times 10^{-7}-0.3 \times 10^{-6}$	1.0-3.0	7-24	0.02-0.20	5.0-15.0	0.44-3.10	2.2-10.0	0.48-1.85	0.46-1.98	0.18-1.21

	Specific Conduct. (μmhos/cm)	Hydrogen Ion Activity (moles/l)	Acidity (mg/l as Ca CO$_3$)	Alkalinity (mg/l as CaCO$_3$)	Iron (mg/l)	Sulfate (mg/l)	Nitrate (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Potassium (mg/l)
Site 190											
Mean	34.79	0.39×10^{-6}	2.37	4.46	0.08	7.82	0.97	3.58	0.61	0.76	0.46
Std.Dev.	4.07	0.74×10^{-6}	0.94	1.56	0.03	2.72	0.42	1.18	0.19	0.29	0.14
Range	30-40	0.4×10^{-7}-0.4×10^{-5}	0.8-5.0	2-9	0.02-0.16	3.0-13.0	0.28-2.00	2.1-8.3	0.35-1.00	0.38-1.54	0.18-0.80
Site 191											
Mean	40.41	0.21×10^{-6}	2.40	6.70	0.07	6.62	1.35	4.06	0.72	0.89	0.61
Std.Dev.	5.12	0.28×10^{-6}	1.10	1.87	0.03	2.50	0.45	1.07	0.21	0.25	0.34
Range	28-56	0.6×10^{-7}-0.2×10^{-5}	1.5-5.8	1-11	0.02-0.16	2.0-12.0	0.77-2.60	2.4-8.6	0.40-1.42	0.46-1.60	0.18-2.12
Site 200											
Mean	29.59	0.37×10^{-5}	3.04	2.48	0.10	7.32	0.90	2.76	0.58	0.68	0.43
Std.Dev.	3.33	0.61×10^{-5}	0.92	0.97	0.14	2.27	0.43	1.69	0.18	0.26	0.15
Range	24-36	0.3×10^{-6}-0.3×10^{-4}	1.5-4.6	1-5	0.02-0.80	3.0-13.5	0.25-2.34	0.3-10.9	0.35-1.14	0.33-1.17	0.18-0.79
Site 410											
Mean	32.66	0.16×10^{-5}	3.10	3.15	0.08	7.70	0.99	2.94	0.65	0.70	0.44
Std.Dev.	3.19	0.19×10^{-5}	0.94	1.12	0.03	2.41	0.40	0.75	0.16	0.25	0.11
Range	27-40	0.6×10^{-7}-0.8×10^{-5}	2.0-6.0	2-7	0.02-0.16	2.0-13.0	0.33-2.00	0.3-4.0	0.39-1.07	0.31-1.34	0.18-0.67
Site 420											
Mean	38.21	0.30×10^{-4}	7.66	0.63	0.11	8.10	0.97	1.95	0.51	0.47	0.39
Std.Dev.	4.56	0.96×10^{-5}	1.45	1.55	0.04	2.12	0.37	0.47	0.15	0.23	0.09
Range	31-51	0.8×10^{-5}-0.5×10^{-4}	4.5-11.0	0-8	0.03-0.18	3.0-13.5	0.17-1.70	0.2-2.7	0.31-0.95	0.27-1.24	0.18 0.57
Site 430											
Mean	48.44	0.44×10^{-4}	11.31	0.02	0.09	9.34	1.11	1.59	0.51	0.50	0.47
Std.Dev.	5.12	0.12×10^{-4}	1.51	0.10	0.04	2.54	0.49	0.43	0.18	0.31	0.36
Range	37-62	0.2×10^{-4}-0.7×10^{-4}	9.0-14.5	0-1	0.03-0.20	3.0-15.0	0.32-2.68	0.2-2.2	0.32-0.95	0.22-1.50	0.18-2.23

	Specific Conduct. (μmhos/cm)	Hydrogen Ion Activity (moles/l)	Acidity (mg/l as Ca CO$_3$)	Alkalinity (mg/l as CaCO$_3$)	Iron (mg/l)	Sulfate (mg/l)	Nitrate (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Potassium (mg/l)
Site 440											
Mean	49.43	0.59×10^{-4}	10.44	0.00	0.16	9.58	1.20	1.65	0.44	0.41	0.44
Std.Dev.	7.65	0.13×10^{-4}	3.47	0.00	0.05	2.57	0.49	0.48	0.14	0.17	0.21
Range	38-72	$0.3 \times 10^{-4}-0.8 \times 10^{-4}$	4.0-21.0	0-0	0.08-0.27	3.0-14.5	0.42-2.68	0.2-2.7	0.20-0.74	0.21-1.15	0.18-1.26
Site 450											
Mean	56.00	0.85×10^{-4}	12.32	0.02	0.22	10.18	1.20	1.34	0.36	0.44	0.39
Std.Dev.	12.81	0.23×10^{-4}	3.79	0.10	0.07	3.11	0.52	0.42	0.12	0.20	0.17
Range	32-98	$0.3 \times 10^{-4}-0.1 \times 10^{-3}$	7.0-25.0	0-1	0.10-0.40	5.0-20.0	0.34-2.34	0.2-2.3	0.2-2.3	0.21-1.01	0.15-0.83
Site 500											
Mean	27.52	0.73×10^{-5}	3.71	1.89	0.11	7.16	0.80	2.03	0.50	0.61	0.38
Std.Dev.	3.18	0.47×10^{-5}	1.23	0.92	0.14	2.36	0.41	0.53	0.14	0.29	0.12
Range	23-34	$0.1 \times 10^{-5}-0.2 \times 10^{-4}$	2.0-8.0	0-4	0.02-0.60	3.0-14.5	0.20-1.80	0.2-2.7	0.31-0.83	0.27-1.67	0.18-0.71
Site 501											
Mean	30.00	0.28×10^{-5}	2.82	2.36	0.05	6.62	1.20	2.51	0.59	0.54	0.39
Std.Dev.	3.39	0.19×10^{-5}	0.78	0.64	0.02	2.66	0.57	0.61	0.16	0.17	0.15
Range	25-37	$0.8 \times 10^{-6}-0.8 \times 10^{-5}$	1.5-4.5	1-4	0.02-0.12	2.0-14.0	0.31-1.05	0.3-3.4	0:35-0.93	0.31-1.17	0.18-0.95
Site 510											
Mean	33.30	0.13×10^{-4}	5.30	1.29	0.05	6.57	1.11	1.83	0.55	0.44	0.39
Std.Dev.	4.09	0.73×10^{-5}	1.18	0.55	0.01	2.46	0.45	0.49	0.15	0.21	0.23
Range	26-40	$0.5 \times 10^{-5}-0.5 \times 10^{-4}$	3.0-8.0	0-3	0.02-0.10	2.0-14.0	0.29-2.00	0.3-2.6	0.30-0.93	0.26-1.16	0.15-1.41
Site 511											
Mean	26.33	0.39×10^{-5}	3.09	1.97	0.07	6.88	0.87	1.94	0.58	0.47	0.45
Std.Dev.	2.90	0.24×10^{-5}	0.94	0.67	0.02	2.65	0.55	0.55	0.17	0.18	0.16
Range	20-33	$0.1 \times 10^{-5}-0.1 \times 10^{-4}$	2.0-5.0	1-4	0.02-0.12	2.0-14.5	0.30-1.05	0.2-3.1	0.39-0.96	0.22-1.05	0.18-0.95

	Specific Conduct. (μmhos/cm)	Hydrogen Ion Activity (moles/l)	Acidity (mg/l as Ca CO_3)	Alkalinity (mg/l as $CaCO_3$)	Iron (mg/l)	Sulfate (mg/l)	Nitrate (mg/l)	Calcium (mg/l)	Magnesium (mg/l)	Sodium (mg/l)	Potassium (mg/l)
Site 520											
Mean	29.89	0.24×10^{-4}	6.28	0.66	0.08	7.41	0.76	1.38	0.37	0.52	0.34
Std.Dev.	4.09	0.90×10^{-5}	1.28	0.72	0.03	2.53	0.47	0.42	0.11	0.32	0.09
Range	23-39	$0.1 \times 10^{-4}-0.5 \times 10^{-4}$	3.0-9.0	0-2	0.02-0.13	2.0-15.0	0.17-2.00	0.2-2.0	0.20-0.64	0.16-1.67	0.18 0.60
Site 530											
Mean	18.86	0.46×10^{-4}	9.18	0.00	7.79	0.88	1.05	0.31	0.51	0.32	
Std.Dev.	3.70	0.13×10^{-4}	1.20	0.00	0.03	2.21	0.70	0.28	0.16	0.29	0.26
Range	29-46	$0.2 \times 10^{-4}-0.8 \times 10^{-4}$	6.5 x 12.0	0-0	0.01-0.13	3.0-15.0	0.5-3.80	0.2-1.7	0.12-0.99	0.16-1.33	0.09-1.53
Site 531											
Mean	37.00	0.39×10^{-4}	8.19	0.19	0.09	7.78	0.90	1.32	0.40	0.46	0.36
Std.Dev.	5.02	0.11×10^{-4}	1.98	0.42	0.03	2.40	0.47	0.43	0.22	0.23	0.28
Range	29-48	$0.2 \times 10^{-4}-0.6 \times 10^{-4}$	5.5-13.5	0-2	0.02-0.16	3.0-14.0	0.20-1.90	0.1-2.0	0.20-1.35	0.16-1.11	0.15-1.65
Site 540											
Mean	22.29	0.15×10^{-4}	4.78	1.28	0.09	6.29	0.73	1.12	0.35	0.51	0.41
Std.Dev.	2.58	0.72×10^{-5}	1.51	0.73	0.04	2.64	0.51	.36	0.11	0.35	0.41
Range	18-29	$0.3 \times 10^{-5}-0.3 \times 10^{-4}$	3.0-9.0	0-3	0.02-0.22	2.0-14.0	0.15-2.00	0.1-2.0	0.20-0.64	0.16-1.82	0.92-2.47